

A PRACTICAL GUIDE TO
IRON AND STEEL WORKS
ANALYSES

WITH SUPPLEMENT

BEING

*SELECTIONS FROM "LABORATORY NOTES ON
IRON AND STEEL ANALYSES"*

BY

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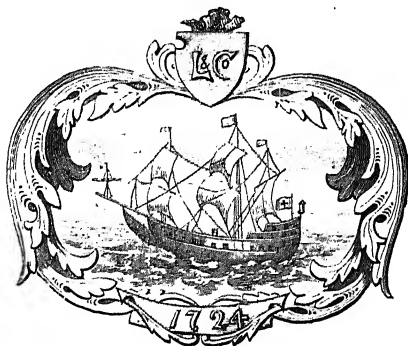
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PREFACE TO FIRST EDITION.

THIS Guide has been compiled from the successful volume, *Laboratory Notes on Iron and Steel Analyses*, to meet the requirements of those who do not wish to enter for the complete analytical course.

Notes on Fuel Analyses have been added.

WEDNESBURY, *December*, 1910.

PREFACE TO EDITION WITH SUPPLEMENT.

IN view of the increasing importance of Alloy Steels, additional selections from the Author's "Laboratory Notes" have been added to the present issue.

The most recent methods for the analysis of Cobalt Steels have been incorporated. A table of contents of the Supplement will be found on page 183.

COUNTY METALLURGICAL AND
ENGINEERING INSTITUTE,
WEDNESBURY, *November*, 1918.

EXTRACT FROM THE PREFACE

TO

LABORATORY NOTES ON IRON AND STEEL ANALYSES.

THESE notes were in the first instance written for the guidance of the staff in an iron and steel works laboratory, which was for some years under the supervision of the author, and where the results of over 40,000 estimations were annually placed on record.

The methods required to be reliable and rapid so as to control and keep pace with the manufacturing operations. It was necessary that all the analysts should work on identical lines. By estimations made at intervals on standard substances, uniform results were regularly obtained from all the members of the staff in the laboratory. The accuracy of the methods was tested in daily practice, and confirmed by analysts acting on behalf of buyers and sellers at home and on the Continent.

The general aim of the book has been to set out the complete course of an assay or an analysis in full detail. In many cases whole paragraphs have

been reintroduced, where necessary, to obviate the confusion arising from cross references.

The analytical methods are given in detail, precise quantities are stated, and the most convenient sizes of beakers, &c., are specified. In these there is no intention of imperiousness. Time and money can be saved by avoiding the waste due to the use of unnecessary excess of chemicals. Good results have been obtained in every-day practice by implicitly following the instructions embodied in the notes. But they must be followed thoughtfully : no book of directions can be a substitute for brains.

Examples of calculations are freely given throughout the notes, as these have been found to be helpful.

The preparation of the necessary solutions is dealt with in a separate part of the book. This arrangement has many advantages.

July, 1909.

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ATOMIC WEIGHTS

USED IN THIS BOOK.

	Chemical Symbol.	Atomic Weight.		Chemical Symbol.	Atomic Weight.
Aluminium, . .	Al	27.1	Molybdenum, . .	Mo	96.0
Arsenic, . .	As	75.0	Nickel, . .	Ni	58.7
Barium, . .	Ba	137.4	Nitrogen, . .	N	14.04
Cadmium, . .	Cd	112.4	Oxygen, . .	O	16.0
Calcium, . .	Ca	40.1	Phosphorus, . .	P	31.0
Carbon, . .	C	12.0	Potassium, . .	K	39.15
Chlorine, . .	Cl	35.5	Silicon, . .	Si	28.4
Chromium, . .	Cr	52.1	Silver, . .	Ag	107.9
Cobalt, . .	Co	59.0	Sodium, . .	Na	23.0
Copper, . .	Cu	63.6	Sulphur, . .	S	32.06
Fluorine, . .	F	19.0	Tantalum, . .	Ta	181.0
Hydrogen, . .	H	1.0	Titanium, . .	Ti	48.10
Iodine, . .	I	127.0	Tungsten or		
Iron, . .	Fe	55.9	Wolfram, . .	W	184.0
Magnesium, . .	Mg	24.36	Vanadium, . .	V	51.2
Manganese, . .	Mn	55.0			

ATOMIC WEIGHTS, REVISED 1909.

Iodine,	126.92	Silicon,	28.3
Manganese,	54.92	Sulphur,	32.07

LABORATORY NOTES

ON

IRON AND STEEL ANALYSES.

ANALYSIS OF STEEL.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample to be tested is treated exactly in the same manner, and the solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

NOTES ON THE PROCESS.

The standard steel ought to have a composition approximating to that of the sample.

Siemens steel should be tested against Siemens steel, basic Bessemer steel against basic Bessemer steel, &c.

The standard and the sample steels should preferably have undergone the same thermal and mechanical treatment.

The mechanical condition of the standard and the sample should not differ widely.

A steel containing a high percentage of carbon requires more acid than one which contains a low percentage of carbon. A high-carbon steel requires to be heated during solution longer than a low-carbon one. But, obviously, both standard and sample ought to be treated with an equal amount of acid, and be heated for the same length of time.

The graduated Eggertz' tubes should be capable of containing 20 c.c. They should be of clear glass, and the bore of each should be equal to others of the same set. Each Eggertz' tube should have a ground glass stopper, or be bent at the top (see p. 158).

The amount of cold solution should be between 3 and 8 c.c. This reservation is now ignored.

The amount of carbon found by the colour test

may differ from that found in the same piece of steel after reheating, annealing, or other treatment.

Certain metals, such as chromium, copper, and nickel, interfere with the accuracy of the colour test for carbon.

In works' practice, the percentage of carbon in a steel is, as a rule, approximately known before being handed in to the laboratory. A suitable standard can therefore be chosen. If, however, the percentage of carbon in the standard differs too much from that of the steel which is being tested, another standard steel should be taken and a fresh comparison made.

The quantity of steel and acid taken for a test should, in some degree, correspond to the percentage of carbon present.

Suitable quantities are :—

For very soft steel, such as is produced for electrical purposes, with carbon under 0·05 per cent., it is advisable to work on 0·3 gramme of the sample dissolved in 5 c.c. of 1·2 specific gravity nitric acid.

For ordinary mild steel, as supplied for structural purposes, with about 0·18 per cent. of carbon, 0·2 gramme may be weighed off and treated with 3·5 c.c. of 1·2 specific gravity nitric acid.

For medium steel—for rails, tyres, axles, &c., containing from about 0·3 to 0·6 per cent. of carbon—0·1 gramme of steel and 2 c.c. of 1·2 specific gravity nitric acid may conveniently be used.

For tool steels, with carbons ranging from 0·75 to

1.5 per cent., 0.10 gramme of the steel dissolved in 5 c.c. of 1.2 specific gravity nitric acid are convenient quantities.

In every case the weighed-off standard and sample should be treated with a like quantity of acid, and under exactly similar conditions.

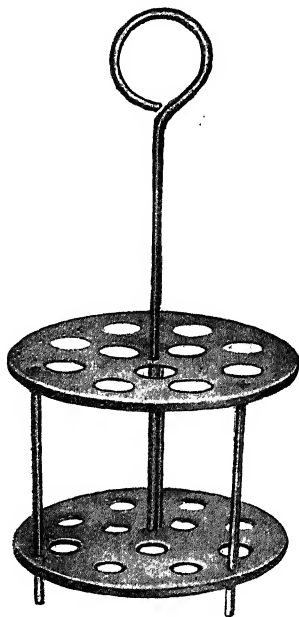


Fig. 1.—Rack for test tubes.

Details of the Process.—Weigh off a convenient quantity of a suitable standard steel, prepared as directed on pp. 11 and 12.

Transfer the weighed quantity to a 13×1.3 cm.

(about 5-inch \times $\frac{1}{2}$ -inch) clean, dry test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

The test tube may be conveniently placed in the kind of rack shown in Fig. 1.

Weigh off a similar quantity of each sample of steel which is to be tested.

All drillings and turnings must be clean, and free from scale, oil, &c.

Transfer each weighed portion to a separate test tube, and note the sample number on each label.

To each weighed quantity measure the required volume of 1.2 specific gravity nitric acid.

When brisk action has ceased, set the test tube rack, with contents, in a bath of boiling water, and keep the bath at boiling point until all the steels are dissolved.

Take the test tube rack and contents from the hot bath, and set to cool in a dish of cold water.

When the solutions have cooled, proceed to compare the relative depths of colour.

The stand shown in Figs. 2 and 3 is useful. It provides a rack for the Eggertz' tubes, supports for the burette from which the acid is measured, support for the burette from which the water for dilution can be conveniently added, and a frame for carrying a light diffuser. A thin pane of ground glass may be fitted, or a piece of filter paper may be gummed on to the frame, or a pane of clear glass may be fitted, to which a piece of wet filter paper may be fastened—it will

easily be made to adhere—before making colour comparisons. A small cutting of rubber tubing is placed at the bottom of each tube recess to act as a pad. Over each burette an inverted test tube is placed to keep out dust.

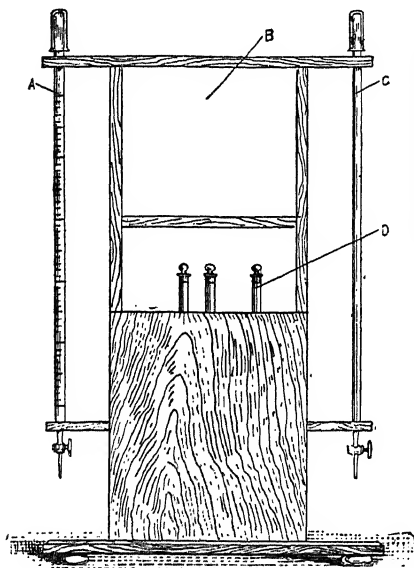


Fig. 2.—Stand for Eggertz' tubes—
Front view.

A, Burette for measuring acid.

B, Frame for light diffuser.

C, Burette for water.

D, Eggertz' tube.

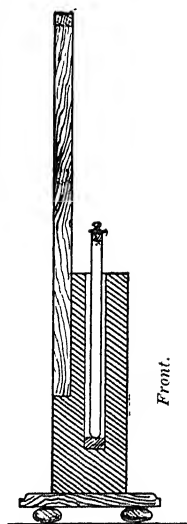


Fig. 3.—Stand for
Eggertz' tubes—
Cross section.

To compare the coloured solutions, pour from the standard test tube into a graduated Eggertz' tube which has a distinguishing mark, such as a rubber

ring or a mark made with a diamond. With a fine jet of cold water rinse the test tube, and drain the rinsings into the graduated tube.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Transfer the solution from the other test tube to a corresponding Eggertz' tube. Rinse, drain, and mix as before.

Compare the depth of colour of the two solutions.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versa*—during the comparison.

Dilute the darker coloured solution with cold water, mix well and compare again.

If necessary, dilute further, mix and compare. Repeat until the solution from the sample is of the same depth of tint as that of the standard.

Read off the volumes of the solutions, and calculate the result.

GENERAL RULE FOR CALCULATING.—Divide the percentage carbon of the standard steel by the volume of its solution, and multiply the result by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0.21 per cent. of carbon, and the solution was diluted to 6.3 c.c. The solution from the sample required to be diluted to 5.4 c.c.

$$\text{Then} \quad \frac{0.21}{6.3} \times 5.4 = 0.18.$$

0.18 = percentage of carbon in the sample, as shown by the colour test.

It is usual to dilute the solution from the standard steel to such a volume that the percentage of carbon in the sample can be directly read off, or so that only a simple calculation is necessary.

EXAMPLE.—Standard steel contained 0.51 per cent of carbon, and the solution was diluted to 5.1 c.c.

The solution from the sample required to be diluted to 5.7 c.c.

∴ Percentage of carbon in the sample, as shown by the colour test = 0.57 per cent.

In the first example the solution from the standard steel was purposely diluted so that every 0.1 per cent. of carbon had 3 c.c. of liquid = 30 measures for each 1 per cent.—

$$\frac{6.3}{30} = 0.21.$$

Similarly, we divide the number of c.c. to which the solution from the sample was diluted—

$$\frac{5.4}{30} = 0.18.$$

0.18 = percentage of carbon in the sample.

RAPID ESTIMATION OF CARBON IN
FURNACE SAMPLES.

A sample of the "metal" is taken from the furnace in a "spoon," allowed to solidify, hammered, cooled, and drilled. The drillings are quickly tested by:—

Weighing off a suitable quantity of the drillings, dissolving in dilute nitric acid, using a small Bunsen burner to hasten the action of the acid, cooling under a water tap, transferring to an Eggertz' tube and comparing with a suitable standard. For very soft steels, it is not unusual to take 0.5 gramme of the drillings, and, having dissolved and cooled, diluting to about 20 c.c., and comparing in long Eggertz' tubes.

ESTIMATION OF MINUTE QUANTITIES OF CARBON.

J. E. Stead described* a new method for the estimation of minute quantities of carbon. This consists in adding solution of potash or soda to the nitric acid solution. The depth of colour is about two and a half times that of the acid solution.

The estimation is carried out thus: 1 gramme of the steel or iron to be tested is weighed off and placed in a 200 c.c. beaker, and, after covering with a watch-glass, 12 c.c. of nitric acid of 1.2 specific gravity are added. The beaker and contents are then placed on a warm plate, heated to about 90° to 100° C., and there allowed to remain until dissolved, which does not usually take more than ten minutes. At the

* *Journal of The Iron and Steel Institute*, No. 1, 1883, p. 213.

same time, a standard steel containing a known quantity of carbon is treated in exactly the same way, and when both are dissolved, 30 c.c. of hot water is added to each and 13 c.c. of standard solution of sodium hydrate of 1.27 specific gravity.

The contents are now to be well shaken, and then poured into a glass measuring-jar and diluted till they occupy a bulk of 60 c.c. After again well mixing and allowing to stand for ten minutes in a warm place, they are filtered through dry filters, and the filtrates, only a portion of which is used, are compared. This may be done by pouring the two liquids into two separate measuring tubes in such quantity or proportion that upon looking down the tubes the colours appear to be equal.

Thus if 50 mm. of the standard solution is poured into one tube, and if the steel to be tested contains, say, half as much as the standard, there will be 100 mm. of its colour solution required to give the same tint. The carbon is, therefore, inversely proportional to the bulk compared with the standard, and in the above assumed case if the standard steel contained 0.05 per cent. carbon, the following simple equation would give the carbon in the sample tested:—

$$\frac{0.05 \times 50}{100} = 0.025.$$

In the same interesting paper Stead describes a simple but efficient instrument for colour estimations. See pp. 158 and 159.

PREPARATION OF STANDARD STEEL FOR
COLOUR TEST.

Procure a billet of steel of average composition and containing a suitable percentage of carbon. The steel selected must not have been overheated or subjected to any treatment having a tendency to alter the condition of the carbon—at least not more than superficially. On one side of the billet drill, with a broad drill, a series of holes of depth enough to permit the drill to more than clear a quarter of an inch below the surface.* Reject these drillings.

With a smaller drill continue for a short distance in. to drill a little from each of the holes. Collect these drillings. Drill a little more out of each hole and collect the drillings. If drilling is continued too long in any hole, the drillings become pulverised and worthless. The pulverising action increases with the depth of the hole, so that it is advisable to begin operations on another side of the billet rather than drill too deeply.

Care must be taken to keep oil and dust from the drillings.

When enough drillings have been collected, the finer portions and the rougher portions are separated by sifting, and are rejected. The remainder should

* If more convenient the billet may be planed or turned rather than drilled, but all surface planings or turnings must be rejected.

be very well mixed and put away in a clean, dry, well-stoppered bottle; the stopper and neck being covered with india-rubber or parchment, and kept in a dry place. From that stock small quantities may be taken from time to time for daily use.

The percentage of carbon in the standard may be accurately ascertained by combustion, and should be compared with standards in use in good steel works and public laboratories.

ESTIMATION OF SILICON IN STEEL.

Outline of the Process.—When mild steel containing silicon is dissolved in hydrochloric acid, and the solution is evaporated to thorough dryness, the silicon becomes oxidised. On boiling the dried residue in hydrochloric acid, all the other components of ordinary mild steel are dissolved. The insoluble residue is collected on a filter, washed, dried, ignited, and weighed, and the percentage calculated.

If there is reason to suspect that the weighed residue is not pure silica (SiO_2), it may be fused with potassium bisulphate, washed, ignited, &c.

Details of the Process.—Weigh off 4.702 grammes of the sample.

Transfer the weighed portion to a 13×11.5 cm. (about 5-inch \times 4½-inch) Jena or Bohemian* beaker.

Add 40 c.c. of hydrochloric acid of 1.16 specific gravity. This is of the specific gravity usually sold.

Evaporate on a hot plate to dryness. The residue should be well dried, but not "burnt" (see note on "hot plate," p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

* The size of beaker specified here and in other pages is not imperative. But it is more satisfactory to state a convenient size than to print "a medium-sized beaker."

with liquid, add 50 c.c. of hot water and 35 c.c. of hydrochloric acid of 1.16 specific gravity.

Boil for a few minutes to dissolve the ferric chloride, &c. Add about 80 c.c. of hot water.

Filter, using a 9 cm. Swedish filter.

Carefully remove the last granules of silica from the inside of the beaker on to the filter, using a "bobby" (a glass rod with a rubber tip) if necessary.

Wash the residue on the filter three or four times with dilute hydrochloric acid—1 of specific gravity 1.16 acid to 6 of water.

Wash several times with hot water.

All traces of colour should be removed from the filter paper and the precipitate. If washing does not effect this, the residue must be purified by fusion (see next page for details).

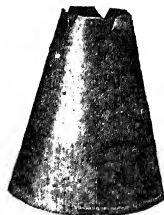


Fig 4.—Filter dryer.

If the residue is white, or of a grey tint on account of a little finely-divided graphite, dry it by placing the funnel with filter paper and contents on a filter dryer (Fig. 4), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter paper in a tared platinum or porcelain crucible or capsule.

In a hot muffle furnace (Fig. 5) burn off the filter paper, and ignite for about half an hour.

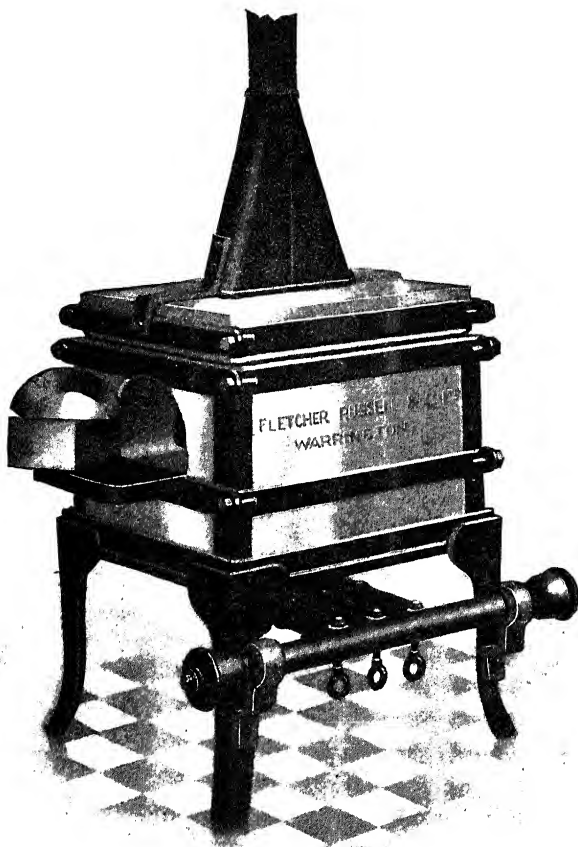


Fig. 5.—Muffle furnace.

Withdraw the crucible, &c., and allow to cool in a desiccator.

Weigh quickly, and note the weight.

Examine the ignited residue, and, if necessary, purify by fusion.

Purification by Fusion.—Place the dried precipitate and paper in a $1\frac{1}{2}$ -oz. platinum crucible, and burn off the paper. Put also into the crucible about 3 grammes of potassium bisulphate, and stir up with a platinum wire. Brush any adhering matter into the crucible. Cover with about $1\frac{1}{2}$ grammes more of potassium bisulphate, and fuse the whole, gently at first, keeping up the temperature as long as white fumes are evolved.

When the crucible has cooled a little, set it on its side in a deep porcelain basin, 5 inches diameter, and pour hot water into the basin. When the melt has loosened, take out the crucible and wash the contents into the basin. Stir well so as to dissolve as much of the sulphate as possible. Filter through a 12.5 cm. Swedish filter paper. Wash until all traces of sulphate are removed. Sometimes about 1 litre of water is required.

Dry the washed precipitate, ignite, allow to cool in a desiccator, and weigh quickly.

Calculate the percentage.

The ignited pure residue (SiO_2) contains 47.02 per cent. of silicon, and when 4.702 grammes of

sample are operated on, the factor for calculation is

$$\frac{47.02}{4.702} = 10.$$

EXAMPLE—

Grammes.

Weight of silica + ash + crucible	=	17.1354
„ crucible . . .	=	17.1312
„ silica + ash . . .	=	0.0042
„ ash	=	0.0007
„ silica	=	<u>0.0035</u>

$0.0035 \times 10 = 0.035 =$ percentage of silicon in the sample.

If a quantity other than 4.702 grammes be taken for analysis, calculate thus—

$$\frac{\text{Weight of silica} \times 47.02}{\text{Weight of sample taken}} = \text{percentage of silicon.}$$

$$\text{Log } 47.02 = 1.6722826.$$

ESTIMATION OF PHOSPHORUS IN STEEL.

THE MOLYBDATE METHOD.

Outline of the Process.—The phosphorus in the weighed portion of the sample is oxidised to phosphoric acid, which can, in a properly regulated solution, form a precipitate, $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$, containing a definite percentage of phosphorus. The precipitate is collected, washed, dried, and weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation. If the weight of the precipitate exceeds 0.3 gramme its composition may be irregular.

Details of the Process.—For mild and medium steels which are free, or practically free, from arsenic.

Weigh off 2 grammes of the drillings.

Transfer the weighed portion to a 14 × 13 cm. (about 5½ × 5-inch) spouted Jena or Bohemian beaker. A wide beaker facilitates evaporation; a tall beaker minimises risk of loss by spirting.

Add 20 c.c. of 1.42 specific gravity nitric acid along with 7 c.c. of water. Higher carbon steels require more acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149). When, towards the end of the evaporation, there is much danger of loss by spitting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for five minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 15 c.c. of 1.16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much as possible. The solution and washings should not measure more than 15 c.c.

Add 17 c.c. of ammonium nitrate solution (see p. 163).

Heat to about 90° C.

Immediately raise the thermometer about 2.5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 15 c.c. of molybdate solution (see p. 102) into the flask. This

will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Rinse any remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1.42 specific gravity) to 50 of water.

Open out the filter paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate into a tared porcelain basin or a basin of platinised nickel—see note on p. 150.

Evaporate on the water bath (Fig. 6) till the precipitate is completely dried.

This water bath consists of an oblong copper box with inlet. On the top are two openings cut to suit the size of the evaporating basins. Copper covers are provided for these openings. These have openings to suit the test tubes required for dissolving a few samples of steel for carbon estimations. The water supply is stored in a Winchester quart or other glass bottle which is fitted with a two-hole rubber stopper. Glass tubing is arranged as shown in the illustration. To start the bath, the bottle is nearly filled with water, the stopper, with the tubes, is placed in position and set on the wooden stand. On

blowing into the curved glass tube, water is forced through the syphon tube into the water bath, into which it will continue to flow till it rises to the level of the bottom of the curved

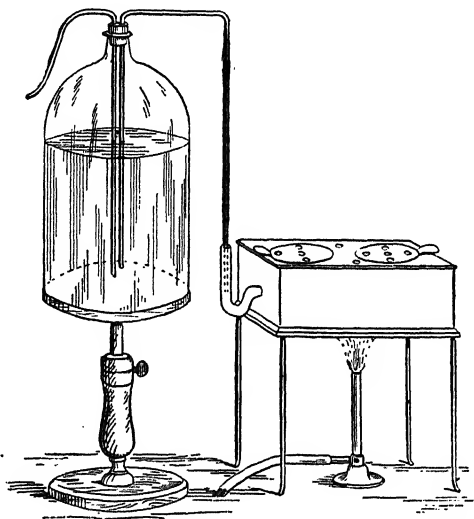


Fig. 6.—Water bath, with constant level water supply.

tube. The water level in the bath will remain practically constant until the supply is exhausted. The bath is mounted on an iron stand, and heat is applied from a Bunsen burner.

Wipe the outside of the basin and allow it to cool. Weigh, and calculate the result.

Other plans are (*a*) to use counterpoised filter-papers, (*b*) to brush the dried precipitate

on to a tared watch-glass, and (c) to estimate by standardised solutions. The author prefers to wash the precipitate into the tared basin and dry it on the water bath.

The yellow precipitate, when thoroughly dried on a water bath, contains 1.63 per cent. of phosphorus, and when 2 grammes of sample are operated on the factor for calculation is

$$\frac{1.63}{2} = 0.815.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate	= 23.184
„ basin . . .	= 23.125
„ precipitate . . .	= <u>0.059</u>

$0.059 \times 0.815 = 0.048$ = percentage of phosphorus in the sample.

$$\text{Log } 0.815 = \bar{1}.9111576.$$

When phosphorus in steel is estimated in strict accordance with the foregoing details, the result may be accepted as reliable.

The following modification has advantages, but requires practice to ensure concordant results:—

Weigh off 2 grammes of the drillings.

Transfer the weighed portion to a 10.2×7 cm. (4-inch \times $2\frac{3}{4}$ -inch) beaker.

Add 40 c.c. of 1.20 specific gravity nitric acid.

Heat till the drillings are dissolved.

Add 10 c.c. of a 1 per cent. solution of potassium permanganate.

Boil till the brown precipitate has dissolved and the pink colour has disappeared.

Cautiously add sulphurous acid (see p. 172) till the solution becomes clear.

Boil off the slight excess of acid and allow to cool.

Add 20 c.c. of 0.88 specific gravity ammonia solution.

Add strong nitric acid till the liquid in the beaker turns to a light sherry colour.

Add not less than 25 c.c. of molybdate solution—prepared by dissolving 100 grammes of ammonium molybdate in 1 litre of water—and, immediately after, add 6 c.c. of strong nitric acid.

The precipitate soon settles, and is filtered, washed, and weighed as in the method described on p. 20.

ESTIMATION BY TITRATION.

Instead of weighing the yellow phosphomolybdate precipitate, it is convenient, when a large number of determinations are to be made, to estimate the phosphorus volumetrically. For this purpose wash the precipitate six times with the usual 2 per cent. nitric acid solution, and afterwards with a 2 per cent. solution of sodium sulphate till free from acid. Open out the filter-paper, and, with a fine-jet wash-bottle containing hot water, wash the precipitate off the paper into a beaker. Measure, from a burette, standard sodium hydrate solution till the precipitate is dissolved, then run in a slight

excess, and note the amount used. Add two or three drops of phenol-phthalein solution to act as an indicator. Then measure, from a burette, standard sulphuric acid or nitric acid solution till change of colour is effected. The solution in the beaker should, of course, be constantly stirred during the addition of the standard acid.

The nitric acid solution may be standardised by pure sodium carbonate (Na_2CO_3), and the caustic soda solution then standardised by the nitric acid. Or, having ascertained the relative strengths of the acid and alkaline solutions, the latter may be standardised by titrating the solution from 2 grammes of steel of known percentage of phosphorus.

Walter Rosenhain states* that when the precipitate is washed with water alone the results agree closely with those obtained on washing with nitric acid and ammonium nitrate. His comparative figures show that water-washing gives a slightly higher result.

RAPID ESTIMATION OF PHOSPHORUS IN FURNACE SAMPLES.

For the very rapid approximate estimation of phosphorus in the "metal" in a basic furnace, two previously-prepared solutions are required, viz.:—

No. 1 solution, made by dissolving 200 grammes of ammonium nitrate in about 150 c.c. of hot water, allowing to cool, adding 250 c.c. of strong nitric acid (say 1.4 specific gravity), and making up to 500 c.c.

* *Iron and Steel Institute Journal*, vol. i., 1908.

No. 2 solution, made by dissolving 50 grammes of ammonium nitrate in about 200 c.c. of hot water, allowing to cool, adding 40 grammes of ammonium molybdate dissolved in 200 c.c. of water, and making up to 500 c.c.

A sample of the "metal" is taken from the furnace in a "sample spoon," allowed to solidify, hammered, cooled, drilled, and quickly tested thus:—

Weigh off 0.2 gramme of the drillings.

Transfer the weighed portion to a 15 cm. \times 1.6 cm. (about $6 \times \frac{5}{8}$ inch) test tube.

Add 4 c.c. of No. 1 solution.

Heat till the drillings are dissolved.

Add 4 c.c. of No. 2 solution.

Warm the solutions.

Shake the tube to facilitate the precipitation.

Compare with the amount of the precipitate from a like quantity of a steel of known percentage of phosphorus which has been similarly treated in a corresponding test tube.

MOLYBDATE AND MAGNESIA METHOD.

For check analyses, especially in disputed cases, it is advisable to employ a good alternative method, and the one in which the product weighed at the end is pure magnesium pyrophosphate, is, with care and experience, reliable.

Outline of the Process.—A weighed quantity of the sample is dissolved in nitric acid, and evaporated to dryness and roasted. The dried mass, containing the phosphorus in its most highly oxidised

state, is dissolved in acid and neutralised. Nitric acid, ammonium nitrate, and molybdate solutions are added to cause the precipitation of a yellow compound $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the other constituents of the steel. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate $(\text{Mg}_2\text{P}_2\text{O}_7)$ which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 14×13 cm. (about $5\frac{1}{2} \times 5$ inch) spouted Jena or Bohemian beaker.

Add 40 c.c. of 1.42 specific gravity nitric acid, along with 10 c.c. of water.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149). When, towards the end of the evaporation, there is much danger of loss by spirting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for ten minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

with liquid, add 35 c.c. of 1.16 specific gravity hydrochloric acid, and allow to boil until the contents of the beaker have dissolved.

Continue the boiling till the bulk of the solution has been reduced to about one-half.

Neutralise the excess acid by cautiously adding ammonia liquor.

Add more ammonia liquor to form a slight permanent precipitate.

Dissolve the precipitate by adding 1.42 specific gravity nitric acid, and stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 2.5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, about 33 c.c. of molybdate solution (see p. 402) into the beaker. This will cause the formation of a yellow precipitate containing the phosphorus.

Stir the solution vigorously to hasten precipitation.

Allow to settle at a temperature under 100° C. for about fifteen minutes.

Pour the solution with the yellow precipitate into a 9 cm. close-texture filter. Rinse any remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1.42 specific gravity nitric acid to 50 of water, collecting the filtrate and washings in a beaker.

Remove the beaker containing the filtrate and washings, and place a clean 350 c.c. (about 12-oz.) conical flask under the funnel.

Dissolve the precipitate by means of a dilute

solution of ammonia—say 1 of 0·880 specific gravity ammonia liquor to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0·880 specific gravity ammonia liquor

Add about 5 c.c. of magnesia mixture (see p. 167).

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate, $Mg(NH_4)PO_4 \cdot 6H_2O$. Allow the precipitate to settle for about an hour.

Decant the clear solution through a 12·5 cm. Swedish filter, and with ammonia water (1 of ammonia 0·880 specific gravity ammonia liquor to 8 of water) wash the precipitate into the filter.

Wash six times with ammonia water as above.

Test the last washings with acidulated silver nitrate (see p. 381).

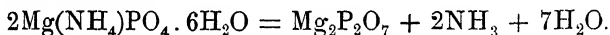
Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be

white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper.

During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), thus—



Withdraw the capsule and contents and place in a desiccator to cool.

Weigh, and calculate.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus.

When 5 grammes of sample are operated on, the factor for ascertaining the percentage is—

$$\frac{27 \cdot 838}{5} = 5 \cdot 568.$$

$$\text{Log } 5 \cdot 568 = 0 \cdot 7456992.$$

EXAMPLE—

Weight of capsule + ash + precipitate	=	16·3348
„ capsule	=	16·3242
„ ash and precipitate	=	0·0106
„ filter ash	=	0·0008
„ precipitate ($\text{Mg}_2\text{P}_2\text{O}_7$)	=	<u>0·0098</u>
$0 \cdot 0098 \times 5 \cdot 568 = 0 \cdot 0546.$		

And 0·055 = percentage of phosphorus in the sample of steel.

66992

801

N19

ESTIMATION OF PHOSPHORUS IN STEELS CONTAINING ARSENIC.

From oxidised solutions of steel which contained arsenic and phosphorus the molybdate solution can precipitate compounds of both together.

The late Mr. Walter G. McMillan pointed out that the presence of 0.01 per cent. of arsenic, if converted into the yellow molybdate precipitate, would calculate out in round numbers as 0.004 per cent. of phosphorus.*

By Prof. Eggertz' method ammonia-phospho-molybdate precipitate free from arsenic may be obtained by precipitating at 40° C., and allowing the precipitate four hours to settle out. The precipitation is not, however, always complete at 40° C. At higher temperatures arsenic is precipitated.

John E. Stead, F.R.S., pre-precipitates the arsenic as sulphide, filters off the solution containing the phosphorus, and in the concentrated filtrate precipitates the phospho-molybdate in boiling solution. His instructive details are, by kind permission, appended.†

METHOD FOR THE DETERMINATION OF PHOSPHORUS.

By J. E. STEAD.

The method employed for the determination of phosphorus is that known by the name of "The Molybdic Acid Process," in which the phospho-

* *Iron and Steel Institute Journal*, vol. i., 1895, p. 139.

† Report of International Committee submitted to the New York meeting of the Iron and Steel Institute, October, 1904.

molybdate of ammonia after precipitation is weighed and the amount of phosphorus calculated from the weight obtained.

In practice we use two modifications of this method, one in which the steel is dissolved in nitric acid (1.20 sp. gr.), solution decolourised by permanganate of potash, and after the addition of a sufficient quantity of nitrate of ammonia the phosphorus is precipitated with molybdate of ammonia, and the precipitate weighed on a tared filter-paper. This system is very useful for steels containing practically no arsenic and silicon.

In the other method precautions are taken to separate any arsenic which might be present.

4.89 grammes of the steel are dissolved in 35 c.c. of nitric acid of 1.42 specific gravity, and 25 c.c. of hydrochloric acid. The solution is evaporated to dryness, taken up with hydrochloric acid, a little water is added, and afterwards pure granulated zinc in quantities sufficient to completely reduce the ferric chloride to ferrous chloride. When the excess of zinc is dissolved, a few drops of ammonium sulphide are added and the solution is violently agitated. If the black sulphide of iron is not completely dissolved, a little more hydrochloric acid must be added until solution is effected. Sulphide of arsenic precipitates at once and coagulates on shaking, and may be filtered off after vigorous agitation or after standing overnight. After filtering, the residue contains the silica and sulphide of arsenic, the filtrate the phosphorus. The filtrate is oxidised with nitric acid after boiling

off the free sulphuretted hydrogen, and the bulk of liquid is reduced to about 70 c.c. by evaporation. After cooling by placing the beaker in cold water, strong ammonia is added until the solution is just neutral, then 8 c.c. of the same ammonia in excess. Nitric acid is now added until the hydrated oxide of iron has just passed into solution, and a final addition of 5 c.c. nitric acid is added. If the volume of liquid is greater than 100 c.c. it may be evaporated until reduced to that bulk. When boiling, 20 c.c. of a 10 per cent. solution of molybdate of ammonia in water* are added, and the beaker with contents well shaken and allowed to stand on the table to allow the phospho-molybdate of ammonia to completely separate. When the supernatant liquid is perfectly bright, and the precipitate has settled to the bottom, the solution is filtered through tared filter-papers. These latter are made in the following manner, viz.:—Two folded papers, after thoroughly drying in a water oven, are placed on opposite pans of an accurately adjusted balance. From the heavier paper portions are clipped off the apex until one filter counterpoises the other. They are then returned to the water oven for fifteen to twenty minutes. They are then taken out, and final and accurate adjustment made. The whole filter is placed inside the other, and in this the precipitate is collected.

After washing the precipitate with water containing 1 per cent. nitric acid, it is given three

* Please note that this solution differs from the one directed to be used for other phosphorus estimations.

washings with distilled water. The filter with contents is then dried at about 110° C.

After drying thoroughly, the filters are separated, the counterpoise paper being placed on one pan, and the paper with precipitate on the other. Weights are added to the pan with the counterpoise paper until equilibrium is established. The weight thus obtained divided by three gives the exact percentage of phosphorus present in the original metal.

ESTIMATION OF MANGANESE IN STEEL.

GRAVIMETRIC METHOD.

Outline of the Process.—The weighed sample of the steel is dissolved, and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a bulky precipitate consisting of basic hydrate and acetate of iron is formed, and the solution containing the manganese is separated on filtering and washing. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, manganese hydrate is precipitated. This is collected, washed, and ignited. The percentage of manganese is ascertained from the weight of the finished residue of Mn_3O_4 .

This method of estimating manganese has been objected to on the ground that the ignited precipitate may vary in composition. With care this need not be so, and the process, as here detailed, is regularly employed in leading iron and steel works for the estimation of manganese in steels, spiegel-eisen, and ferro-manganese. A process which yields concordant results over such a wide range—results acceptable alike to buyers and sellers—cannot consistently be classed as unreliable.

Details of the Process.—Weigh off 2 grammes of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 15 c.c. of 1.42 specific gravity nitric acid along with 7 c.c. of water. Prof. Arnold recommends hydrochloric acid for dissolving tool steel.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 20 c.c. of hot water, and boil.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after violent shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 35 c.c. of ammonium acetate solution (see p. 162).

From this point the process is also applicable to the gravimetric estimation of manganese in pig iron.

Boil briskly over the flame of a 16 mm. (about $\frac{5}{8}$ -inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is risky.

Prepare a 28 cm. (about 11-inch) folded filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large

filter stand—see Fig. 7. Set under it a 1,200 c.c. (about 40-oz.) Phillips' conical beaker on a dry cork mat.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove the flask till the brisk action ceases, replace on the tripod, and allow the rapid boiling to continue. It

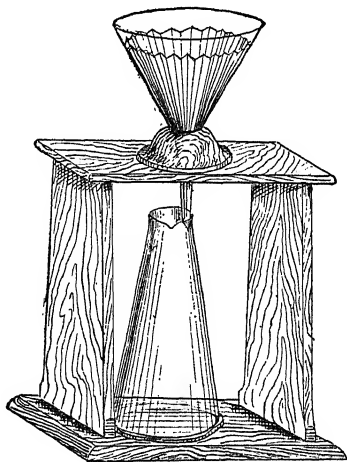


Fig. 7. —Stand, &c., for large funnel.

may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear colourless liquid should drain away quickly when on the filter.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking

care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask twice with hot water and pour the rinsings on to the filter. Allow the liquid to drain off thoroughly into the beaker flask.

Wash three times with hot water, collecting the washings in the beaker flask. If the operations have proceeded smoothly, filtering and washing may easily be completed within an hour.

Cool the filtrate and washings.

Add about 4 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about 15 minutes after brominating.

Cautiously add about 30 c.c. of strong ammonia solution.

Stir well, and allow to stand for a few minutes.

Boil till most of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off the excess ammonia.

Filter through a 12.5 cm. Swedish filter-paper, and wash four times with hot water.

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace

which is at a white heat. Allow to remain in the hot muffle for 30 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Correction for Co-precipitated Iron.

A small quantity of ferric oxide usually accompanies the manganese oxide, and may be easily estimated by colour, in the following manner:—

Transfer the weighed substance to a 60 c.c. (about 2-oz.) Bohemian beaker.

Add about 10 c.c. of hydrochloric acid, and boil till the precipitate has dissolved.

Add about 5 c.c. of a 10 per cent. ammonium sulpho-cyanide solution.

If the mixture shows only a faint colouration, no correction is necessary.

If the mixture shows a decided colour, add about 10 c.c. of cold water, and pour the solution into a 100 c.c. stoppered graduated cylindrical measure. Rinse the beaker, and pour the rinsings into the measure. Mix well.

Measure 20 c.c. of standard iron solution ($= 0.0005$ gramme of ferric oxide, see p. 408) into a corresponding stoppered graduated glass having a distinguishing mark. Add 5 c.c. of the 10 per cent. sulpho-cyanide solution, and mix well.

Compare the depth of colour of the solutions.

Dilute the more highly-coloured solution, so as to bring each to the same depth of colour.

Calculate the weight of the co-precipitated ferric oxide, thus—

Divide the weight of ferric oxide in the standard solution by its volume, and multiply the product by the volume of the solution of the oxides from the manganese estimation.

EXAMPLE.— Fe_2O_3 in standard solution = 0.0005 gramme diluted to 25 c.c.

Solution of oxides diluted to 40 c.c.

$$\frac{0.0005}{25} \times 40 = 0.0008.$$

0.0008 = weight of co-precipitated ferric oxide.

Calculate the percentage of manganese.

On igniting the precipitate as directed, the manganese peroxide is converted into Mn_3O_4 . Mn_3O_4 contains 72.052 per cent. of manganese, and when 2 grammes of sample have been operated on the factor for calculation is

$$\frac{72.052}{2} = 36.026.$$

EXAMPLE—

	Gramme.
Weight of $\text{Mn}_3\text{O}_4 + \text{Fe}_2\text{O}_3 + \text{filter ash}$	= 0.0164
„ filter ash	= 0.0008
„ $\text{Mn}_3\text{O}_4 + \text{Fe}_2\text{O}_3$	= 0.0156
„ Fe_2O_3	= 0.0008
„ Mn_3O_4	= 0.0148

$0.0148 \times 36.026 = 0.53 = \text{percentage of manganese in the sample of steel.}$

$$\text{Log } 36.026 = 1.5566160.$$

ESTIMATION OF MANGANESE IN STEEL.

COLORIMETRIC METHOD

suggested by Mr. Hugh Marshall. Details of process by Mr. Harry E. Walters, Duquesne Steel Works.*

Outline of the Process.—When steel containing manganese is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour is developed, the depth of which depends on the amount of manganese present. This is compared with the colour from an equal weight of steel containing a known percentage of manganese.

Details of the Process.—Weigh off a suitable quantity of the sample. If the steel is supposed to contain 0.75 per cent., or over, 0.1 gramme should be taken; if the supposed percentage is less, 0.2 gramme should be weighed off.

Transfer the weighed portion to an 18×1.6 cm. (about $7 \times \frac{5}{8}$ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add to each 10 c.c. of nitric acid of 1.2 specific gravity. If 0.1 gramme of steel has been taken, 6 c.c. of nitric acid will suffice.

Place the test tubes in a water bath (see Fig. 6, p. 21), and heat until the steels have dissolved and all nitrous fumes are driven off.

Add 15 c.c. (or 10 c.c. for 0.1 gramme of steel) of a 0.133 per cent. solution of silver nitrate (= 0.02

* Proceedings of Engineers' Society of Western Pennsylvania.

gramme of AgNO_3 in 15 c.c.). This will cool the solution to the temperature at which the next reagent should be added.

Immediately add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 163).

Continue heating in the water bath till oxidation commences, then for about half a minute longer.

Remove the tubes from the bath while the evolution of gas continues, and place them in a cold-water bath.

When the solutions have cooled, transfer the coloured solution from the standard steel to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer the coloured solution from the other steel to a corresponding Eggertz' tube, and compare with the standard solution.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versa*—during the comparison.

Dilute the darker coloured solution with cold distilled water as far as necessary, mix well, and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage of manganese in the standard steel by the volume of its solution, and multiply the product by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0·52 per cent. of manganese, and the solution was diluted to 20·8 c.c. The solution from the sample of steel being tested required to be diluted to 23·2 c.c.

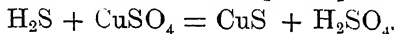
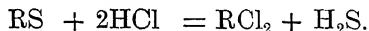
$$\text{Then } \frac{0\cdot52}{20\cdot8} \times 23\cdot2 = 0\cdot58,$$

and $0\cdot58 =$ percentage of manganese in the sample of steel.

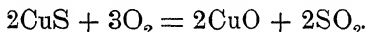
ESTIMATION OF SULPHUR IN STEEL.**EVOLUTION AND GRAVIMETRIC METHOD.**

Outline of the Process.—The weighed sample is placed in a properly-fitted evolution flask, and acid is added so as to cause the sulphur to be converted into sulphuretted hydrogen, which, as it bubbles through a solution of copper sulphate, forms a precipitate of copper sulphide. The sulphide is separated on a filter, washed thoroughly, dried, ignited, and the residue weighed.

The reactions may be conveniently summarised in the following equations, when $R = \text{Mn}$ or Fe :—



The washed and dried copper sulphide, on being strongly heated with access of air, is oxidised.



From the weight of the copper oxide the quantity of sulphur which was present is deduced.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask which has been fitted with a rubber cork carrying a safety funnel, condenser, and delivery tube arranged as shown in Fig. 8 (see next page).

Moisten the cork, and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of cold saturated solution of copper sulphate into a 7-inch \times 1-inch (18×2.5 cm.) test tube or beaker.

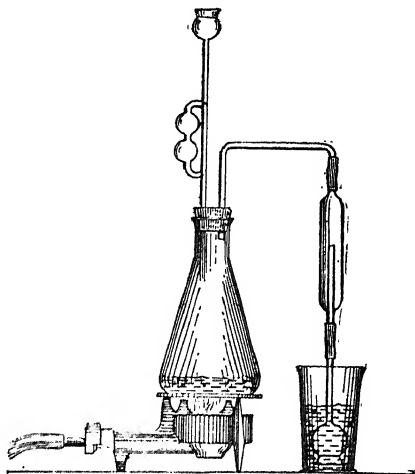


Fig. 8.—Flask, &c., for sulphur evolution.

Arrange the apparatus so that the condensing delivery tube dips into the solution.

Pour about 40 c.c. of 1.16 specific gravity pure hydrochloric acid into the safety funnel.

If necessary, lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of acid into the flask.

A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the burner—still permitting the gases to come off through the copper sulphate solution—and allow to remain there until all the steel has dissolved, and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube.

Filter off the copper sulphide, using a 12.5 cm. Swedish (but not an "ashless") filter.

Wash any adhering sulphide from the delivery tube on to the filter.

Wash the copper sulphide about twelve times with hot water. This precipitate should be washed quickly. It is difficult to wash all the copper sulphate through an ordinary filter; it is more difficult to wash it from an "ashless" filter.

Dry the precipitate and filter.

Ignite in a tared porcelain capsule, at first gently in a muffle, and then for 30 minutes in a moderately hot part of the muffle.

Allow the crucible and contents to cool in a desiccator.

Weigh, and calculate the percentage of sulphur in the steel.

EXAMPLE.—Weight of sample taken = 5 grammes.

Weight of capsule + ash + precipitate	= 8.3143
„ capsule	= 8.3070
„ ash + precipitate	= 0.0073
„ ash	= 0.0008
„ precipitate	= 0.0065

Atomic weight of sulphur = 32.06.

Molecular weight of CuO = 63.6 + 16 = 79.6.

$$\frac{32.06}{79.6} = 0.402764.$$

0.402764 = weight of S deduced from weight of CuO.

The factor for 5 grammes is

$$\frac{100}{5} \times 0.402764 = 8.0553.$$

Weight of ignited precipitate = 0.0065.

$0.0065 \times 8.055 = 0.052$ = percentage of sulphur in the sample of steel.

It is not unusual to make a duplicate estimation on either 4 or 6 grammes.

Factor for 4 grammes = 10.07.

„ 6 „ = 6.71.

ESTIMATION OF SULPHUR IN STEEL.

VOLUMETRIC (IODINE) METHOD.

Outline of the Process.—The sulphur is evolved as sulphuretted hydrogen, which is caught in a solution of caustic soda or caustic potash. This is afterwards more than neutralised with sulphuric acid, and titrated with standard iodine solution, starch being used as an indicator.

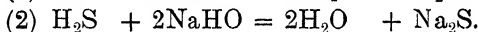
The changes which take place are :—

(1) The sulphur present, as sulphide, combines with hydrogen of the acid used for dissolving the steel, and sulphuretted hydrogen is evolved.

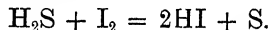
(2) The sulphuretted hydrogen is caught in caustic alkali solution, and held there as alkaline sulphide.

(3) On the caustic liquid being acidified, sulphuretted hydrogen is again formed, and is retained in the solution.

When R = Mn or Fe the reactions may be thus expressed :—



The quantity of sulphur present is then estimated as a result of the reaction :—



Addition of iodine in excess of that required for the completion of the reaction gives a permanent blue colour with starch solution.

STANDARDISING THE IODINE SOLUTION.—Having prepared the solutions, the iodine solution is standardised thus :—

Weigh off 5 grammes of steel drillings containing a known percentage of sulphur.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask, which is fitted with a rubber cork carrying a safety funnel and a delivery tube.

Moisten the cork and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of the prepared caustic soda solution (see p. 415) into a beaker or an 18 cm. \times 2.5 cm. (about 7-inch \times 1-inch) test tube.

Arrange the apparatus so that the condensing delivery tube dips into the solution, as shown in Fig. 8, p. 44.

Pour about 40 c.c. of pure 1.16 specific gravity hydrochloric acid into the safety funnel. Lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of the acid into the flask. A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the

burner—still allowing the gases to come off through the caustic soda or potash solution—and allow to remain there until all the steel has dissolved and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube, and rinse it into a 7-inch porcelain basin.

Empty the solution from the beaker or test tube into the same basin.

Wash the beaker or test tube, collecting the washings also in the basin.

Add 30 c.c. of dilute sulphuric acid (see p. 172) and about 5 c.c. of the freshly-prepared but cold starch solution (see p. 171).

From a burette filled to zero, carefully run standard iodine solution (see p. 166) into the basin while stirring briskly. When a decided violet colour appears which is somewhat persistent, add the iodine solution carefully drop by drop, and, when a distinct violet colour remains for about a minute after the addition of one of the drops, read off and note the volume of iodine solution used.

Correction for Quantity of Iodine Solution required to show Colour in the Solutions used.

Into a 7-inch porcelain basin put

About 50 c.c. of the caustic soda solution.

„ 30 c.c. of the dilute sulphuric acid solution.

„ 50 c.c. of cold, distilled water, and

„ 5 c.c. of the starch solution.

Run in, cautiously, standard iodine solution (stirring meanwhile), until a violet colour of the

same depth as in the other basin appears and remains.

Read off the quantity taken, and deduct from the quantity used in the former titration.

Duplicate the sulphur estimation, using 4 grammes of the steel.

If the results are fairly concordant, they may be accepted; if the difference is too great, make another estimation, using $4\frac{1}{2}$ grammes of the steel.

CALCULATION FOR STANDARDISING.

5 grammes of the steel (which was known to contain 0.046 per cent. of sulphur) required 9.4 c.c. of the standard iodine solution, and the blank experiment required 0.3 c.c.

∴ The H_2S from the steel required = 9.1 c.c.

$$\frac{0.046 \times 5}{100} = 0.0023.$$

$$\frac{0.0023}{9.1} = 0.0002527 = \text{result of 1st estimation.}$$

7.43 c.c. (after correction for blank) of the standard iodine solution were required for 4 grammes of the steel.

$$\frac{0.046 \times 4}{100} = 0.00184.$$

$$\frac{0.00184}{7.43} = 0.0002476 = \text{result of 2nd estimation.}$$

Result of 1st estimation = 0.0002527.

Result of 2nd estimation = 0.0002476.

Average of the two estimations = 0.0002502.

The bottle containing the solution is therefore labelled "Standard iodine solution: every c.c. = $\cdot 0002502$ gramme of sulphur. Deduct for blank $0\cdot 3$ c.c."

If the solution is kept in stock for a time, it should be restandardised before using again. If in regular use, restandardise every third day.

ESTIMATION OF SULPHUR IN A SAMPLE OF STEEL BY THE VOLUMETRIC (IODINE) METHOD.

Weigh off 5 grammes of fine drillings taken through such a depth of the sample as required for a fair average.

Proceed exactly as in standardising.

Note the volume of the standard iodine solution required, and deduct the volume required for the blank.

Duplicate on 4 grammes

Calculate the results.

EXAMPLE OF CALCULATION.—5 grammes of the steel sample required $10\cdot 1$ c.c. of the standard iodine solution.

The blank was $\cdot 33$, therefore the standard iodine solution required for the sample steel was $9\cdot 77$ c.c.

Every c.c. of the iodine solution = $\cdot 0002502$ gramme of sulphur.

$$\frac{\cdot 0002502 \times 100 \times 9\cdot 77}{5} = \cdot 005004 \times 9\cdot 77 =$$

$0\cdot 049$ = percentage of sulphur in sample of steel.

CADMIUM AND IODINE METHOD.

Instead of using a solution of caustic soda, the evolved sulphuretted hydrogen may be caught in a solution of cadmium chloride prepared as directed on p. 404. Cadmium sulphide is precipitated, and is afterwards dissolved and estimated by titrating with standard iodine solution. The apparatus is fitted up as shown in Fig. 8 (p. 44), except that a larger beaker is employed to hold the 20 c.c. of 2 per cent. cadmium chloride solution and 200 c.c. of cold water. 5 grammes of the sample are treated with acid and water, and the gases evolved are led into the cadmium chloride solution. When evolution is complete, 10 c.c. of cold starch solution and 25 c.c. of 1.16 specific gravity hydrochloric acid are added to the contents of the beaker. For starch solution see p. 171.

When the whole is cold, standard iodine solution (see p. 166) is measured in till a permanent blue colour is obtained.

An advantage of this method is that one may, with practice, approximately gauge the percentage of sulphur in the sample before titrating.

The procedure, precautions, method of standardising, and calculating are all as described in the preceding pages.

At the National Physical Laboratory, Bushy Park, London, the volumetric estimation of sulphur is carried out thus:—The steel drillings are dissolved in the evolution flask of this apparatus in hydrochloric acid of 1.10 specific gravity, the operation being aided

* Rosenhain, *Iron and Steel Institute Journal*, vol i., 1908.

by heat, although boiling the acid is avoided. The evolution flask and entire apparatus are filled, prior to the commencement of the operation, with an atmosphere of carbon dioxide, obtained by passing a stream of this gas, derived from a cylinder of liquid carbonic acid, through the entire apparatus. The evolved gases, aided towards the end of the operation by a further stream of carbonic acid, are bubbled through an absorption flask containing a solution of cadmium acetate strongly acidified with acetic acid (25 grammes pure cadmium acetate and 10 per cent. glacial acetic acid per litre); after passing this flask the gases pass through a narrow-bore tube of vitreous silica heated to redness by a Bunsen burner with a flat flame, the gases passing finally through a second cadmium acetate absorption flask and then away to the furnace-chamber. When the steel has completely dissolved, the contents of the two absorption flasks are mixed and the yellow sulphide of cadmium is filtered off; this is a rapid operation since the flask need not be washed carefully—the operation is merely intended to separate the sulphide from the bulk of the absorption liquid. As soon as this has been done the precipitate is washed from the filter back into the original flask, and there dissolved in 10 c.c. of standard iodine solution, the action being aided by the introduction of a small quantity of hydrochloric acid. The excess of iodine is then titrated by means of sodium thio-sulphate and starch. It is to be observed that while this titration can be carried out in the liquid of the absorption flasks without filtration, it has been found that this leads to occasional discrepancies in the

results. Apparently, particularly in the case of high-carbon steel, the evolved gases carry into the absorption flask something which is capable of absorbing iodine, but which is not sulphur; this disturbing substance can be eliminated by the filtration described above.

The following table, which contains typical examples from a wide range of steel, shows the closeness of the agreement observed between the results of this evolution method and the oxidation method:—

Steel.	Lab. No.	Percentage of Sulphur found by	
		Evolution.	Gravimetric.
Tyre, . .	896	0·042	0·044
Tyre, . .	936	0·046	0·049
Tyre, . .	952	0·045	0·049
Shaft,	0·041	0·043
Tyre, . .	969	0·014	0·013
Plate, . .	980	0·048	0·045
Joist, . .	1018	0·054	0·052
Joist, . .	1054	0·062	0·063

ESTIMATION OF SULPHUR BY OXIDATION AND PRECIPITATION AS BARIUM SULPHATE.

Outline of the Process.—The weighed sample is dissolved in acid and oxidised. It is again dissolved, and, on addition of barium chloride solution, barium sulphate is precipitated. This is collected on a filter, washed, dried, and weighed. From the ascertained weight the percentage of sulphur is calculated.

Details of the Process.—Weigh off 3 grammes of the sample.

Transfer to a 3-inch \times 1-inch platinum basin.

Add sufficient concentrated nitric acid, in small instalments, to dissolve the sample. Keep the basin covered with a watch-glass during the period of dissolving.

When completely dissolved, add 2 grammes of potassium nitrate.

Evaporate to dryness.

Ignite at a red heat.

When cool, add 50 c.c. of a 1 per cent. solution of sodium carbonate.

Gently boil for a few minutes.

Filter, collecting the filtrate (and washings) in a 7.5 \times 5 cm. (about 3-inch \times 2-inch) beaker.

Wash with hot 1 per cent. sodium carbonate solution.

Add hydrochloric acid to acidify the filtrate.

Evaporate to dryness.

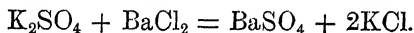
When the beaker has cooled, add 5 c.c. of hydrochloric acid in 45 c.c. of water.

Boil briskly for five minutes.

Filter, collecting the filtrate (and washings) in a 10 \times 7.5 cm. (about 4-inch \times 3-inch) beaker.

Wash thoroughly with hot water containing about 2 per cent. of hydrochloric acid.

Add 5 c.c. of a 10 per cent. solution of barium chloride. This should precipitate all the sulphur as barium sulphate according to the equation—



Filter through a close-texture filter-paper.

Wash well with hot water.

Test some of the last washings by collecting in a clean test tube, and adding a few drops of clear acidified silver nitrate solution.

Wash twice after all the chloride appears to have been washed out.

Dry the precipitate on the filter.

Ignite in a tared crucible for half an hour in a hot muffle.

Weigh and calculate.

EXAMPLE—

	Grammes.
Weight of crucible + ash + precipitate	= 16.8504
„ crucible	= 16.8308
„ ash + precipitate	= 0.0196
„ ash	= 0.0010
„ precipitate (BaSO_4)	= 0.0186

Percentage of S in $\text{BaSO}_4 = 13.73$.

$\frac{13.73}{5} = 2.746 = \text{factor when 5 grammes of sample are taken.}$

$$0.0186 \times 2.746 = 0.051.$$

0.051 = percentage of sulphur in the sample of steel.

ANALYSIS OF PIG IRON.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample of pig iron to be tested is dissolved and filtered, and the filtered solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

Details of the Process.— Weigh off 0.1 gramme of a suitable standard.

As a standard, steel is preferable to pig iron, even against the well-founded belief that steel should be tested against steels of their own class.

Suitable standards:—

For Grey iron,	0.50	per cent.	carbon steel.
„ Mottled iron,	1.00	„	„
„ White iron,	1.40	„	„

Transfer the weighed portion to a clean, dry 13 × 1.3 cm. (5 inches × $\frac{1}{2}$ inch) test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

Weigh off 0.1 gramme of the sample of pig iron to be tested.

Transfer the weighed portion to a similar test tube with a distinctive label or mark on it.

To each weighed quantity add nitric acid solution of 1.2 specific gravity.

If 0.5 standard,	.	.	.	2	c.c.
„ 1.0	„	.	.	2.5	c.c.
„ 1.4	„	.	.	3.0	c.c.

When brisk action has ceased, set the test tubes, with contents, in a bath of boiling water, and keep at boiling point for twenty minutes. The rack and stand shown in Figs. 1 and 2 (pp. 3 and 5) are convenient.

Withdraw the test tubes from the hot bath.

Immediately filter the solution from the pig iron through a 7 cm. filter into a 20 c.c. Eggertz' tube. Rinse the test tube with warm water, collecting the washings, through the filter, in the same Eggertz' tube.

If the solution is not promptly filtered, as directed, a coloured precipitate may settle out and spoil the estimation.

Label the Eggertz' tube.

Allow to cool.

Drain the cold standard solution from the test tube into a corresponding Eggertz' tube, which has a distinguishing mark, such as a rubber ring or a mark made with a diamond. Rinse into the Eggertz' tube with a fine jet of cold water.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Compare the depth of colour of the two solutions.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versa*—during the comparison.

Dilute the darker-coloured solution with cold water, mix well, and compare again.

If necessary, dilute further, mix, and compare.

Repeat until the solution from the sample is of the same depth of tint as that of the standard.

When the solutions in the Eggertz' tubes are of the same depth of colour, read off the volumes of the solutions, and calculate the result.

EXAMPLE.—Standard material contained 0.63 per cent. of combined carbon; solution was diluted to 6.3 c.c.

Sample required to be diluted to 7.8 c.c.

∴ Combined carbon in the sample of pig iron = 0.78 per cent.

For other examples of calculations, see pp. 7 and 8.

ESTIMATION OF GRAPHITIC CARBON IN PIG IRON.

Outline of the Process.—To the weighed sample in a beaker acid is added and evaporated to dryness. During the evaporation the silicon is oxidised to silica. Acid is again added, and, after boiling for a few minutes, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The washed residue is transferred to a tared basin, dried on a steam bath, and the weight ascertained. On ignition, the graphite is burned off, and, after cooling, the fixed residue is weighed. The weight of the graphite is found by difference, and the percentage is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12.5×9.7 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 30 c.c. of 1.16, specific gravity hydrochloric acid.

Evaporate on a hot plate till the residue in the beaker is quite dry (see note on "hot plate," p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of hot water and 15 c.c. of 1.16 specific gravity hydrochloric acid.

Boil until the iron has dissolved.

Filter through a 12.5 cm. Swedish filter.

Wash three times with acidulated water—1 of 1.16 specific gravity hydrochloric acid to 6 of water.

Wash three or more times with hot water.

Allow to drain thoroughly.

With a fine-jet wash bottle wash the insoluble matter from the filter into a tared platinum or porcelain basin of 7.6 cm. (or about 3 inches) diameter.

Evaporate on a water bath, and complete the drying in a steam oven.

Allow to cool in a desiccator.

Weigh and note the weight.

Ignite the residue. Let the basin remain in the muffle until a pure white, or faintly pink or reddish, residue is left. The residue (silica) should be white, but even a slight trace of iron will impart a colour.

Withdraw the basin and contents, and allow to cool until the basin can be lifted by hand.

Complete the cooling in a desiccator.

Weigh again and calculate.

EXAMPLES.—

(a) When the percentage of silicon is not required.

Weight of capsule + residue,	Grammes.
before ignition,	= 27.4374
Weight of capsule + residue, after	
ignition,	= 27.3850
Loss on ignition = weight of graphite	<u>0.0524</u>

2 grammes of sample were taken for estimation.

$$\frac{100}{2} \times 0.0524 = 2.62.$$

2.62 = percentage of graphite in the sample of pig iron.

(b) When the percentage of silicon is required.

EXAMPLE—

Weight of basin + insoluble	Grammes.
matter, after drying, . . .	= 27.4374
Weight of basin	= 27.3185
Weight of insoluble matter, after	
drying (<i>graphite and silica</i>), .	= 0.1189
Weight of basin + insoluble	Grammes.
matter, after ignition, . . .	= 27.3850
Weight of basin	= 27.3185
Weight of insoluble matter, after	
ignition (<i>silica</i>),	= 0.0665

Weight of insoluble matter, before ignition,	Grammes. = 0.1189
Weight of insoluble matter, after ignition,	= 0.0665
Loss on ignition (<i>graphite</i>) . . .	<u>0.0524</u>

To find percentage of graphite (2 grammes taken)—

$$\frac{100}{2} \times 0.0524 = 2.62.$$

2.62 = percentage of graphite.

To find percentage of silicon:—

The ignited pure residue (SiO_2) contains 47.02 per cent. of silicon, and when 2 grammes of sample are operated on, the factor for calculation is

$$\frac{47.02}{2} = 23.51.$$

EXAMPLE—

	Grammes.
Weight of silica + crucible =	18.2783
„ crucible . . . =	18.2118
„ silica . . . =	<u>0.0665</u>

$0.0665 \times 23.51 = 1.56$ = percentage of silicon in the sample.

$$\text{Log } 23.51 = 1.3712526.$$

ESTIMATION OF TOTAL CARBON IN PIG IRON.

- (a) Add together the percentage of combined carbon and of graphitic carbon; or
(b) Estimate by combustion.
-

ESTIMATION OF SILICON IN PIG IRON.

If it is intended to estimate silicon, phosphorus, and manganese in the sample of pig iron, the method described on pp. 74 to 77 should be adopted, but when silicon alone is to be determined the following method is recommended.

Outline of the Process.—When pig iron is dissolved in acid and the solution is evaporated to thorough dryness, the silicon (Si) becomes oxidised to silica (SiO_2). After boiling for a few minutes in hydrochloric acid, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The insoluble residue is collected on a filter, washed, dried, ignited till all the graphite has been burned off, and weighed. The percentage is then calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12.2×9.7 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1.16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p. 149) till the residue in the beaker is quite dry, then allow to stand on the hot plate for about ten minutes more to complete the oxidation of the phosphorus.

Withdraw the beaker and place it on a cork

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of 1.16 specific gravity hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter the solution through a 12.5 cm. Swedish filter-paper.

Wash the residue (silica and graphite) well, first with dilute hydrochloric acid—say 1 of 1.16 specific gravity acid to 6 of water—and afterwards with hot water as often as required.

All traces of colour should be removed from the filter-paper and the precipitate. If washing does not effect this, the residue must be afterwards purified by fusion (see p. 16) or treated with hydrofluoric acid, which causes the volatilisation of silica (see next page).

Dry the residue by placing the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents, and allow to cool in a desiccator.

Weigh quickly and note the weight.

Examine the weighed residue.

If the residue is white, calculate the percentage of silicon in the sample.

If, as sometimes happens, the silica is not quite white, add a few drops of hydrofluoric acid to the contents of the weighed platinum capsule (this must not be done in a porcelain capsule or crucible), carefully evaporate, ignite, allow to cool in a desiccator, and re-weigh.

The percentage of silicon in silica is 47.02, and when 2 grammes of sample are taken for the estimation, the factor for calculating the percentage is—

$$\frac{47.02}{2} = 23.51.$$

$$\text{Log } 23.51 = 1.3712526.$$

EXAMPLES.—

(a) Without the use of hydrofluoric acid.

	Grammes.
Weight of capsule + silica + ash	= 19.1458
„ capsule . . .	= 19.0685
„ silica + ash . . .	= 0.0773
„ filter ash . . .	= 0.0008
„ silica . . .	= 0.0765

$$0.0765 \times 23.51 = 1.799.$$

1.80 \div percentage of silicon in the sample of pig iron.

(b) Using hydrofluoric acid.

Grammes.

Weight of capsule + contents, . = 18.7243

Weight of capsule + impurities
after treatment with hydro-
fluoric acid = 18.6913

0.0330

Add for impurity in the hydro-
fluoric acid, the amount of which
had been previously ascertained
in a like quantity of the acid . = 0.0010

Weight of residue volatilised
= *silica* = 0.0340

Then using the factor (23.51) noted in example (a),

$$0.034 \times 23.51 = 0.799.$$

0.80 \div percentage of silicon in the sample of
white pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

STANDARD METHOD—APPLICABLE TO ALL PIG IRONS EXCEPT SWEDISH AND HEMATITE.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron, except graphitic carbon and silicon, are dissolved and are separated from the insoluble residue (which may be used to ascertain the percentage of silicon) by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the iron. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12.2×9.6 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1.16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149), then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid add 20 c.c. of hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter through a 12.5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 300 c.c. (about 10-oz.) conical flask.

Wash three times with dilute hydrochloric acid—1 of 1.16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. **Silicon may be estimated in the residue.**

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium-nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution and pour, all at once, 175 c.c. of molybdate solution (see p. 162) down the thermometer into the flask.

175 c.c. should be sufficient for a pig iron containing 3 per cent. of phosphorus. For a forge or foundry pig iron 100 c.c. should be enough.

This will cause the formation of a yellow precipitate containing all the phosphorus.

Shake the flask well, and allow the precipitate to settle.

Filter the solution through a 12.5 cm. close-texture filter-paper, collecting the filtrate (and washings) in a beaker.

Wash, once by decantation and afterwards in the usual way, with nitric acid solution—1 of acid (specific gravity, 1.42) to 20 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 500 c.c. beaker.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (0.880 specific gravity) to 8 of water—collecting the solution in the beaker.

Wash four times with dilute ammonia solution and twice with warm water. Collect the washings in the same beaker as the solution. Heat the solution and washings to about 60° C.

Add one-sixth bulk of ammonia liquor (0.88 specific gravity).

Add 25 c.c. of magnesia mixture (see p. 167), and stir well.

Allow the precipitate to settle.

Filter, using a 12.5 cm. Swedish filter-paper.

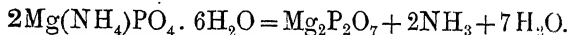
Wash with dilute ammonia solution—1 of am-

monia liquor (specific gravity, 0.88) to 8 of water—until the washings are free from chlorides.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), thus—



Withdraw the capsule, or crucible, and its contents and allow to cool in a desiccator.

Weigh, and note the weight.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27.838 per cent. of phosphorus. When 2 grammes of sample have been operated on the factor for calculation is—

$$\frac{27.838}{2} = 13.919.$$

$$\text{Log } 13.919 = 1.1436080.$$

EXAMPLE—

	Grammes.
Weight of precipitate + filter ash + capsule =	19.9607
„ capsule =	19.7385
„ precipitate + ash =	0.2222
„ ash =	0.0008
„ precipitate. =	<u>0.2214</u>

$$0.2214 \times 13.919 = 3.08.$$

3.08 = percentage of phosphorus in the sample of pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

RAPID METHOD—NOT APPLICABLE TO SWEDISH OR
HEMATITE PIG IRONS.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron—except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings are collected in a 250 c.c. flask, cooled, and made up to definite volume. A measured quantity of solution is withdrawn by a pipette, and transferred to a flask. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the

measured quantity, is collected, washed, dried, and weighed.

Details of the Process.—Weigh off 2 grammes of the sample in the form of drillings or fine turnings.

Transfer the weighed portion to a 12.2×9.6 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1.16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p.149) to dryness, then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 20 c.c. of 1.16 specific gravity hydrochloric acid, and evaporate to about half bulk.

Add 25 c.c. of hot water, and boil for two minutes.

If it is desired to estimate silicon in the washed residue:—

Filter through a 12.5 cm. Swedish filter-paper, collecting the filtrate and washings in a 250 c.c. flask.

Wash three times with dilute hydrochloric acid, say 1 of 1.16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper, and the washings are colourless. With ordinary care the residue can be completely washed without making the volume more than 250 c.c.

Cool the solution, make up to the mark with cold water, and mix well.

If it is not desired to estimate silicon in the washed residue :—

Wash the solution out of the beaker (without filtering) into a 250 c.c. flask.

Cool under a water tap.

Make up to the mark with cold water.

Mix well and allow to settle.

Withdraw from the clear portion of the solution, by means of a pipette, the quantity required for the phosphorus estimation ; or, if the results are required earlier, the measured portion from the pipette may be run through a filter and washed into the precipitating flask.

In either case—

Draw from the 250 c.c. flask enough of the solution to fill the pipette to the mark indicating the quantity which will deliver 20.38 c.c. This is done to clean it. Reject the solution as it runs out.

Draw from the 250 c.c. flask more of the solution into the pipette, and adjust it to the 20.38 c.c. delivery mark.

Run the measured quantity into a 200 c.c. (about 7 ozs) conical flask.

Add 2 c.c. of ammonia liquor.

Neutralise with hydrochloric acid.

Add 17 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution, and add all at once 20 c.c. of molybdate solution (see p. 162), which may be poured down the

lower part of the thermometer into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for one minute or more. While shaking, press the forefinger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Wash any remaining precipitate on to the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1.42 specific gravity acid to 50 of water.

Open out the filter-paper, and, with a fine-spout wash bottle containing warm water, wash the precipitate into a tared porcelain basin or a tared basin of platinised nickel (see note on p. 150).

Evaporate on a water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

Other plans are (*a*) to use counterpoised filter-papers, and (*b*) to brush the dried precipitate on to a tared watchglass, and weigh.

The yellow precipitate, when thoroughly dried on a water bath, contains 1.63 per cent. of phosphorus.

When the solution from 2 grammes is made up to 250 c.c., 20.38 c.c. = 0.163 gramme, and when this

quantity has been used for the estimation, the factor for calculation is

$$\frac{1.63}{0.163} = 10.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate	= 24.669
„ basin	= 24.568
„ precipitate,	= <u>0.101</u>

$$0.101 \times 10 = 1.01.$$

1.01 = percentage of phosphorus in the sample of pig iron.

STANDARD METHOD FOR THE ESTIMATION OF PHOSPHORUS IN HEMATITE OR SWEDISH PIG IRONS.

MOLYBDATE AND MAGNESIA METHOD.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron, except graphitic carbon and silicon, are dissolved and are separated from the insoluble residue (which may be used to ascertain the percentage of silicon) by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the iron. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as

magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 15×11.5 cm. (about $6 \times 4\frac{1}{2}$ inches) Bohemian or Jena beaker.

Add 40 c.c. of 1.16 specific gravity hydrochloric acid along with 20 c.c. of 1.42 specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of 1.16 specific gravity hydrochloric acid and allow to boil until all the iron appears to be dissolved.

Add about 20 c.c. of hot water, and boil briskly for a few minutes more.

Filter through a 12.5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 250 c.c. conical flask.

Wash three times with dilute hydrochloric acid—1 of 1.16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. Silicon may be estimated in the residue.

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 33 c.c. of molybdate solution (see p. 162) into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Cork the flask and shake it vigorously, so as to hasten the precipitation.

Allow to settle at a temperature under 100° C. for about fifteen minutes.

Pour the solution with the yellow precipitate into a 9 cm. close-texture filter, collecting the filtrate (and washings) in a beaker. Wash the remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1.42 specific gravity nitric acid to 50 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 300 c.c. conical flask.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (0.88 specific gravity) to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0.88 specific gravity ammonia liquor. Mix the solutions in the flask.

Add, drop by drop, about 5 c.c. of magnesia mixture (see p. 167). Stir the solution briskly, or agitate the flask, while adding the magnesia mixture.

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate ($\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$).

Allow the precipitate to settle for an hour or two.

Decant the clear solution through a 12.5 c.m. Swedish filter, and with dilute ammonia liquor wash the precipitate into the filter. Collect the filtrate (and washings) in a suitable beaker.

Wash six times with dilute ammonia liquor.

Test the last washings with acidulated silver nitrate (see p. 170).

Wash two or three times with the dilute ammonia liquor after all the chlorides have been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for

an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition the precipitate loses water and is converted into magnesium pyrophosphate = $(Mg_2P_2O_7)$.



Withdraw the capsule or crucible and allow to cool in a desiccator.

Weigh, and calculate the result.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27.838 per cent. of phosphorus.

When 5 grammes of sample are used for the estimation, the factor for ascertaining the percentage is

$$\frac{27.838}{5} = 5.568.$$

$$\text{Log } 5.568 = 1.7456992.$$

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 18.3536
„ capsule	= 18.3472
„ ash and precipitate	= 0.0064
„ filter ash	= 0.0008
„ precipitate $(Mg_2P_2O_7)$	= 0.0056

$$0.0056 \times 5.568 = 0.0312.$$

0.0312 = percentage of phosphorus in the sample of steel.

RAPID (MOLYBDATE) METHOD FOR THE ESTIMATION
OF PHOSPHORUS IN HEMATITE OR SWEDISH PIG
IRONS.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron—except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings are collected and evaporated to small bulk. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the measured quantity, is collected, washed, dried, cooled, and weighed.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 15×11.5 cm. (about $6 \times 4\frac{1}{2}$ inches) Bohemian or Jena beaker.

Add 40 c.c. of 1.16 specific gravity hydrochloric acid along with 20 c.c. of 1.42 specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of 1.16 specific gravity hydrochloric acid.

Boil until all the iron appears to be dissolved.

Add about 10 c.c. of hot water, and continue the boiling for about two minutes.

Allow the residue to subside, and pour the clear yellow liquid through a 12.5 cm. Swedish filter, collecting the filtrate (and washings) in a 9×7.5 cm. (about $3\frac{1}{2} \times 3$ inches) Bohemian or Jena beaker.

Wash the residue into the filter.

Wash three times with water acidulated with 10 per cent. of 1.16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much

as possible. The solution and washings should not measure more than 25 c.c.

Add 25 c.c. of ammonium nitrate solution (see p. 163).

Heat to about 90° C.

Immediately raise the thermometer about 2.5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 25 c.c. of molybdate solution (see p. 162) into the flask. This will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate into a 9 cm. close-texture, smooth-surface filter-paper, collecting the filtrate (and washings) in a suitable beaker. Wash any remaining precipitate on the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1.42 specific gravity) to 50 of water.

Open out the filter-paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate on to a tared porcelain basin or a basin of platinised nickel—see note on p. 150.

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

The yellow precipitate, when thoroughly dried on

a water bath, contains 1.63 per cent. of phosphorus, and when 5 grammes of sample have been used for the estimation, the factor for calculation is

$$\frac{1.63}{5} = 0.326.$$

$$\text{Log } 0.326 = \bar{1}.5132176.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate	= 22.483
„ basin . . .	= 22.387
„ precipitate . . .	= <u>0.096</u>

$$0.096 \times 0.326 = 0.313.$$

0.313 = percentage of phosphorus in the sample.

ESTIMATION OF MANGANESE IN PIG IRON.**GRAVIMETRIC METHOD.**

Outline of the Process.—The weighed sample is treated with acid and evaporated to complete dryness. By this means the silicon is converted into insoluble silica. On the addition of more acid and the application of heat, the insoluble residue from an ordinary pig iron consists of silica and graphite only. The soluble portion is filtered off into a flask, and carefully neutralised. Ammonium acetate is added, and, on boiling, a bulky precipitate of ferric acetate and hydrate is formed. This is separated, by filtering and washing, from the liquid containing the manganese in solution. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, hydrated manganese oxide is precipitated. The precipitate is collected on a filter, washed, dried, and ignited. The percentage of manganese is calculated from the weight of the finished residue of Mn_3O_4 .

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12 cm. \times 12 cm. (about $4\frac{1}{2} \times 4\frac{1}{2}$ inches) Bohemian spouted beaker.

Add 15 c.c. of nitric acid, 1.42 specific gravity, along with 7 c.c. of hydrochloric acid of 1.16 specific gravity.

Evaporate on a hot plate till thoroughly dry (see note on hot plate, p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of nitric acid along with 10 c.c. of water, and set to boil briskly for a few minutes.

Filter the solution through a 12.5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40 ozs.) globular Bohemian flask.

Wash the residue (silica and graphite) three times at least with hot water.

Boil the filtrate and washings.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid, even after vigorous shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 33 c.c. of ammonium acetate solution.

Then follow the details from the corresponding point on p. 35 to the end of the gravimetric process.

ESTIMATION OF MANGANESE IN PIG IRON.

COLORIMETRIC METHOD.

(From a Memo. by PERCY HILL, Wednesbury.)

Outline of the Process.—When manganiferous pig iron in a fine state of division is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour appears, the depth of which depends on the amount of manganese present. The graphite and silica are allowed to settle, and a measured quantity of the clear pink-coloured solution is drawn off and transferred to a 50 c.c. Eggertz' tube. This is compared with the colour from an equal weight of pig iron containing a known percentage of manganese.

For pig irons containing under 1 per cent. of manganese, the colorimetric method for steels (see pp. 40 to 42) works satisfactorily if the graphite and silica are allowed to settle and 5 c.c. are drawn off for the estimation; but, if like quantities of solutions are used for pig irons containing over that percentage of manganese, a precipitate will separate out. This precipitation is avoided if Percy Hill's modification is adopted.

Details of the Process.—Weigh 0.1 gramme of the sample, which must be fine enough to pass through a 100-mesh sieve.

Transfer the weighed portion to an 18×1.6 cm. (about $7 \times \frac{5}{8}$ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add 8 c.c. of nitric acid of 1.2 specific gravity to each.

Place the test tubes in a water bath (see p. 21), and allow them to remain until the iron has dissolved—generally about ten to fifteen minutes.

Add to each, 7.5 c.c. of 0.4 per cent. solution of silver nitrate.

Replace the test tubes with their contents in the water bath, and add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 163).

Continue heating in the water bath until the colour appears, and, while the tubes are still effervescing, remove the tubes and place them in a cold-water bath.

When the solid residues in the tubes have subsided, draw off, with a pipette, 5 c.c. of the clear pink-coloured solution from the standard "pig" to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer a similar quantity of the coloured solution from the sample "pig" to a corresponding Eggertz' tube, dilute, and compare with the standard solution.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through the ground glass or a sheet of moistened filter-paper will pass through the solutions (see Fig. 2, and description of stand on pp. 5 and 6). Change the relative positions of

the tubes—standard tube to the right, and sample tube to the left, and *vice versa*—during the comparison.

Dilute with cold distilled water as far as necessary, mix well, and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage manganese of the standard pig iron by the volume of its solution, and multiply the result by the volume of the solution of the pig iron which is being tested.

EXAMPLE.—Standard pig iron contained 2.35 per cent. of manganese, and the measured portion of its pink-coloured solution was diluted to 23.5 c.c. A similar measure of the pink-coloured solution from the sample required to be diluted to 19.4 c.c.

$$\frac{2.35}{23.5} \times 19.4 = 1.94.$$

1.94 = percentage of manganese in the sample, as shown by colour test.

ESTIMATION OF SULPHUR IN PIG IRON.

EVOLUTION AND GRAVIMETRIC METHOD.

In ordinary pig iron, sulphur is estimated in the manner described for steels in previous pages.

Usually 5 grammes of the sample are taken, and a duplicate estimation is made on 4 or on 6 grammes.

But certain pig irons (notably white irons) do not yield all their sulphur by evolution when dissolved in hot hydrochloric acid. In such cases, M'Farlane & Gregory, of Frodingham,* adopt the following method:—

Weigh off 5 grammes of the sample.

Intimately mix the weighed portion with half a gramme of sulphur-free cream of tartar (potassium-hydrogen-tartrate, $C_4H_5KO_6$).

Wrap the mixture in filter-paper, and place in a crucible, cover the crucible, and place the whole in a muffle which is at a good red heat.

Allow to remain for about fifteen minutes, the muffle being kept at a red heat all the time.

Withdraw the crucible and contents, and, when cool, pound the mixture in a mortar, transfer to a 500 c.c. (about 17 ozs.) conical flask, and proceed with the estimation as detailed on pp. 43 to 54.

When there is occasion to suppose that all the

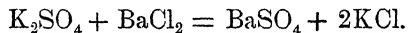
* See *Chemical News*, vol. xciii., p. 201.

sulphur has been evolved, take away the tube or flask through which the gases have been passed, and put another tube or flask with copper sulphate or cadmium sulphate solution in position, and continue the boiling for a few minutes. If a precipitate is formed, add it to that previously obtained. After experience has been gained, this precaution may be unnecessary.

ESTIMATION OF SULPHUR IN PIG IRON.

GRAVIMETRIC METHOD.

Outline of the Process.—A weighed quantity of the sample is treated with acids and with chlorate to dissolve the iron, &c., and to oxidise the sulphur and the silicon. The solution is evaporated to dryness; and more acid is added and evaporated. The dried mass is then boiled in acid, and the insoluble portion is separated by filtration. Barium chloride is added to the clear, hot filtrate. This causes the precipitation of barium sulphate—a reaction indicated by the equation,



Barium sulphate is insoluble in the acid solution. It is collected on a filter, washed, dried, ignited, cooled, and weighed. The percentage of sulphur is then calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 13×10.5 cm. (about 5×4 inches) Bohemian or Jena beaker.

Add 40 c.c. of pure 1.16 specific gravity hydrochloric acid along with 20 c.c. of pure 1.42 specific gravity nitric acid, and heat gently.

When brisk action has ceased, add a few crystals of potassium chlorate, or the chlorate crystals may be previously dissolved in one of the acids.

Evaporate to dryness on a hot plate (see note on hot plate, p. 149), and allow to bake for twenty minutes after.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 25 c.c. of pure 1.16 specific gravity hydrochloric acid, and again evaporate to dryness on the hot plate.

Again withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of pure 1.16 specific gravity hydrochloric acid.

Boil, to dissolve the iron, &c.

Evaporate till a skin begins to form.

Withdraw the beaker and allow it to cool a little.

Add 5 c.c. of pure hydrochloric acid and about 20 c.c. of warm water.

Stir the solution well and immediately decant it into a 12.5 cm. Swedish filter, collecting the filtrate (and washings) in a 13×10.5 cm. (about 5×4 inches) Bohemian or Jena beaker.

Rinse the beaker twice with a little hot water

Decant the liquid into the filter.

Allow the whole to drain into the beaker.

Wash the filter twice with water, and allow the washings to drain into the beaker. The solution and washings should not measure more than 75 c.c.

Remove the beaker and set it on the hot plate.

When the liquid boils, add, drop by drop, 6 c.c. of a 10 per cent. solution of barium chloride.

Place a clock-glass over the beaker and boil the contents briskly for a few minutes.

Place the beaker in a warm place to allow the precipitate to settle.

Decant the liquid into a 12.5 cm. Swedish filter, collecting the filtrate and washings in a clean beaker of suitable size.

Pour about 100 c.c. of hot water and 2 c.c. of hydrochloric acid into the beaker, and shake it so as to mix the liquid and the precipitate.

Allow to settle in a warm place.

Again decant into the filter.

Pour another 100 c.c. of water into the beaker, and shake it so as to mix as before.

Drain the liquid and precipitate into the filter.

Wash several times with water.

Test the last washings with acidulated silver nitrate solution (see p. 170).

Wash twice with water after all chlorides appear to have been washed out.

Place the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14) on a hot plate, and allow to remain till dried.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and content and place in a desiccator to cool.

Weigh, deduct the weight of the filter ash and the weight of barium sulphate in the blank, and calculate the percentage.

The weight of barium sulphate due to impurity in the acids used should be ascertained by a blank estimation, and deducted.

The blank estimation may be made on a mixture of 110 c.c. of the hydrochloric acid and 20 c.c. of the nitric acid. These should be evaporated to small bulk, cautiously diluted with water, boiled, barium chloride solution added, and set aside for twelve hours at least to complete precipitation. The precipitate is collected on a filter, washed, dried, ignited, and weighed. The Winchesters containing the acids should be labelled, and set aside for sulphur estimations only.

It is assumed that the water used does not contain sulphates. If this is not so, a measured quantity of the water, equal to the quantity used for an ordinary estimation, must be included in the blank estimation.

As the amount of the precipitated sulphate in the acids and chlorate is usually very small, precipitation takes place very slowly. To ascertain more quickly, and probably more accurately, the weight of the sulphate due to these, two weighed quantities of a sample of pig iron may be treated with like

quantities of the acids and chlorate, and the barium sulphate estimated by the method detailed above.

An example may make this point more clear:—

Let "blank" represent the BaSO_4 from the acids and chlorate used.

Weight of BaSO_4 from $7\frac{1}{2}$ grammes	
+ blank	= 0.0475 gramme.
Weight of BaSO_4 from $2\frac{1}{2}$ grammes	
+ blank	= 0.0225 ,,
	<hr/>
	0.0250 ,,
	<hr/>

The blank is the same in both cases, since equal quantities of acid and chlorate are used for each. The difference (0.025 gramme), therefore, shows the weight of BaSO_4 from 5 grammes of the sample.

BaSO_4 from 5 grammes	= 0.0250 gramme.
" $7\frac{1}{2}$ " = $0.025 \times \frac{3}{2}$	= 0.0375 ,,
BaSO_4 from $7\frac{1}{2}$ grammes + blank	= 0.0475 gramme.
" $7\frac{1}{2}$ "	= 0.0375 ,,
∴ " blank	= 0.0100 ,,

BaSO_4 from 5 grammes	= 0.0250 gramme.
" $2\frac{1}{2}$ " = $0.025 \times \frac{1}{2}$	= 0.0125 ,,
BaSO_4 from $2\frac{1}{2}$ grammes + blank	= 0.0225 gramme.
" $2\frac{1}{2}$ "	= 0.0125 ,,
∴ " blank	= 0.0100 ,,

Pure BaSO_4 contains 13.73 per cent. of sulphur, and, when 5 grammes are taken for analysis, the factor for ascertaining the percentage is

$$\frac{13.73}{5} = 2.746.$$

$$\text{Log } 2.746 = 0.4387005.$$

EXAMPLE—

Weight of crucible + ash and

	blank + precipitate	=	17.4607 grammes.	
„	crucible . . .	=	17.428	„
			<hr/>	
„	ash + precipitate .	=	0.0179	„
„	filter ash + blank .	=	0.0013	„
			<hr/>	
„	precipitate (BaSO_4)	=	0.0166	„
			<hr/> <hr/>	

$$0.0166 \times 2.746 = 0.046.$$

0.046 = percentage of sulphur in the sample of pig iron.

ANALYSIS OF LIMESTONE.*

The volatile matter is estimated by carefully driving off all that is volatile at a steady red heat, and another sample is treated for general analysis. With one exception—magnesia—the weighed precipitates are of the same composition as the components of the limestone.

The following analysis may be made on a sample which has been finely pounded and dried. Drying, however, is not always necessary—indeed, it is unusual in iron and steel works. But, in the event of a consignment of limestone being very wet, an estimation of the moisture may be made by the method detailed on pp. 254 and 255.

ESTIMATION OF VOLATILE MATTER.

Outline of the Process.—A portion of the sample is weighed into a tared basin, and heated at a steady red heat until all the volatile matter is driven off. After allowing to cool, the basin (with its contents) is re-weighed. The percentage loss is then calculated.

* For analysis of calcined limestone, see p. 309.

Details of the Process.—Tare a 7.6 c.m. (about 3 inches) diameter platinum or porcelain basin, and note the weight.

Weigh into it 0.8 gramme of the finely-powdered sample.

Heat gently near the front of a muffle, taking care not to permit the carrying off of solid particles.

Heat more strongly by pushing the basin and contents to the hottest part of the muffle, and allowing to remain for about an hour. By this treatment the "volatile matter" is driven off.

Withdraw the basin to the slab in front of the muffle, and, when just cool enough to permit removal by hand, place it, with its contents, in a desiccator.

When cold, weigh and calculate.

EXAMPLE—

	Grammes.
Weight of basin	= 18.3775
„ sample	= 0.8000
„ basin and sample before ignition	= 19.1775
„ „ „ after ignition	= 18.8318
Loss of weight = volatile matter . . .	= 0.3457

Then, as 0.8 gramme was taken for the estimation, the loss of weight $\times \frac{100}{0.8}$ = percentage of volatile matter.

$$\frac{0.3457 \times 100}{0.8} = 0.3457 \times 125 = 43.21 = \text{per cent.}$$

of the volatile matter in the sample of limestone.

To make sure that all volatile matter has been driven off, the basin and contents may be reheated in the hottest part of the muffle for an hour, and, after cooling in the desiccator, re-weighed.

The chief constituent of the "volatile matter" is carbon dioxide. Its percentage may be inferred from the result obtained by the following method:—

Weigh into a tared basin 5 grammes of the pounded sample.

Keep the basin and contents in a steam oven at 100° C. for about two hours.

Allow to cool in a desiccator.

The loss of weight = the water driven off; the remainder of the volatile matter may be accepted as carbon dioxide. Occasionally a little organic matter is present.

EXAMPLE—

Water driven off	.	.	.	Grammes.
				= 0.024

$$0.024 \times \frac{100}{5} = 0.48,$$

and 0.48 = percentage of moisture.

Percentage of volatile matter,	.	43.21
" water,	.	0.48
" carbon dioxide,	.	<u>42.73</u>

When required, the percentage of carbon dioxide may be ascertained by means of a Schroedter's apparatus.

ESTIMATION OF INSOLUBLE MATTER.

Outline of the Process.—The weighed portion of the sample is boiled in hydrochloric acid solution, water is added, and the insoluble matter is collected on a filter, washed, dried, ignited, and weighed. From the ascertained weight the percentage is calculated.

Details of the Process.—Weigh off 1 gramme of the finely-pounded sample.

Transfer the weighed portion to a 400 c.c. beaker.

Add about 20 c.c. of warm water, and shake the beaker so as to mix the sample well with the water.

Add 10 c.c. of 1.16 specific gravity hydrochloric acid. If the limestone contains more than traces of iron, about 5 c.c. of nitric acid should also be added to facilitate separation at a subsequent stage.

Set the beaker and contents on a hot plate, and heat to boiling point.

Add about 30 c.c. of hot water.

Boil briskly.

Wash the insoluble residue into a 9 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash thoroughly with dilute hydrochloric acid—say 1 of 1.16 specific gravity acid to 10 of water—and afterwards with hot water.

Dry the residue and filter-paper.

Put the filter-paper and the residue in a tared platinum or porcelain capsule, and place in a hot muffle.

Allow to remain for half an hour.

Withdraw, and, when cool enough to just permit removal by hand, place the capsule and contents in a desiccator.

When cold, weigh.

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 17.3983
„ capsule	= 17.3863
„ ash and precipitate	= 0.0070
„ filter ash	= 0.0007
„ residue	= 0.0063

Then, as 1 gramme was taken for the estimation, the weight of residue $\times \frac{100}{1} =$ percentage of residue.

$0.0063 \times 100 = 0.63 =$ percentage of insoluble residue in the sample of limestone.

The insoluble residue, as a rule, consists largely, if not entirely, of silica. If the percentage of silica is required, it should be estimated after fusion.

ESTIMATION OF ALUMINA.

Outline of the Process.—The filtrate from the separation of the insoluble matter is heated to boiling point, and a slight excess of ammonia liquor is added to precipitate the alumina and any ferric oxide present. Some of the excess ammonia is boiled off, the solution being left faintly alkaline. The precipitate is collected, washed, dried, ignited, and weighed. The percentage is then calculated.

Details of the Process.—To the filtrate from the insoluble matter, add 2 or 3 c.c. of 1.42 specific gravity nitric acid.

Boil.

Add a slight excess of ammonia liquor. This will cause the separation of a gelatinous precipitate of aluminium hydrate. If pure, the precipitate will be white, but if iron is present it will also be precipitated—as reddish-brown ferric hydrate.

Boil until faintly alkaline.

Immediately wash the precipitate on to a 12.5 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash several times with hot water.

Dry the precipitate and filter-paper.

Put the precipitate and filter-paper in a tared platinum or porcelain capsule, and place near the front of a muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for about thirty minutes.

Withdraw the capsule, and, when just cool enough to permit removal by hand, place it in a desiccator.

When cold, weigh.

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 17.3922
„ capsule	= 17.3863
„ ash + precipitate	= 0.0059
„ filter ash	= 0.0008
„ precipitate (Al_2O_3)	= 0.0051

Then, as 1 gramme was taken for the estimation, the weight of $\text{Al}_2\text{O}_3 \times \frac{100}{1} =$ percentage of Al_2O_3 .

$0.0051 \times 100 = 0.51 =$ percentage of alumina in the sample of limestone.

When iron is present in appreciable amount an estimation may be made on a separate portion of the sample. The corresponding weight of ferric oxide should then be calculated and deducted from the total weight of the precipitate, the difference being taken as alumina.

Weight of Fe $\times 1.429 =$ weight of Fe_2O_3 .

ESTIMATION OF LIME.

Outline of the Process.—The filtrate from the separation of the alumina is heated nearly to the boiling point. Ammonia liquor and ammonium chloride are added. A hot solution of ammonium oxalate is then added to precipitate the lime as calcium oxalate. The precipitate is collected on a filter, washed, ignited, and the resulting calcium oxide is weighed. The percentage is then calculated.

Details of the Process.—Heat the filtrate from the separation of alumina to the boiling point.

If there is reason to believe that the sample contains much magnesia, add 10 c.c. of a strong solution of ammonium chloride. This prevents the precipitation of magnesia when ammonium oxalate is added, and checks the solvent action of magnesium chloride on calcium oxalate.

Add about 10 c.c. of 0.88 specific gravity ammonia liquor.

Add 40 c.c. of hot ammonium oxalate [$C_2(NH_4)_2O_4$] solution (see p. 163). This will cause the precipitation of calcium oxalate (C_2CaO_4). The reaction is:—



Continue the boiling for about one minute.

Set the beaker in a warm place to allow the precipitate to subside.

Wash the precipitate on to a 12.5 cm. Swedish filter, collecting the filtrate and washings in a 1,000 c.c. beaker.

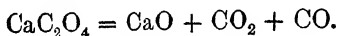
Wash thoroughly with hot water.

Dry the precipitate.

Place the dried precipitate and filter-paper in a tared platinum or porcelain capsule near the front of the muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for forty minutes at least. This will cause the decomposition of the calcium oxalate: carbon monoxide and carbon dioxide will be evolved, while calcium oxide (lime) will remain.

The reaction is:—



Withdraw the capsule, and, when it is just cool enough to be lifted by the hand, place it with its contents in a desiccator.

When cold, weigh.

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 18.9327
„ capsule	= 18.3773
„ ash and precipitate	= 0.5554
„ filter ash	= 0.0008
„ precipitate (CaO)	= 0.5546

Then, as 1 gramme was taken for the estimation, the weight of CaO $\times \frac{100}{1}$ = percentage of CaO.

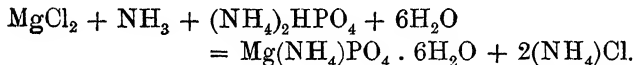
$0.5546 \times 100 = 55.46$ = percentage of CaO in the sample of limestone.

ESTIMATION OF MAGNESIA.

Outline of the Process.—The filtrate from the separation of the lime is heated to about 60° C., and ammonium phosphate solution is added to precipitate the magnesia as ammonium-magnesium-phosphate. This is collected on a filter, washed, dried, carefully ignited, and weighed. From the weight of the resulting magnesium pyrophosphate the percentage is calculated.

Details of the Process.—To the still warm filtrate from the lime estimation add one-tenth bulk of ammonia liquor (sp. gr. 0.88).

Add about 5 c.c. of 20 per cent. ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ solution (see p. 164). If the sample contained magnesia, a white precipitate of ammonium-magnesium-phosphate $[\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}]$ will be formed, the reaction being—



Stir briskly, and allow the precipitate to settle.

Filter through a 12.5 cm. Swedish filter.

Wash about eight times with ammonia water (1 of ammonia liquor (sp. gr. 0.88) to 8 of water),

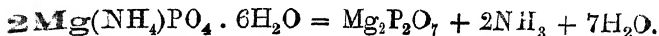
Test the last washings with acidulated silver nitrate (see p. 170).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate and filter.

Ignite, cool, and weigh.

The filter should be thoroughly dried, and the ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses water and is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), thus



EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 17.3946
„ capsule	= 17.3862
„ ash and precipitate . . .	= 0.0084
„ filter ash	= 0.0008
„ precipitate ($\text{Mg}_2\text{P}_2\text{O}_7$) . .	= 0.0076

Magnesium pyrophosphate contains 36.243 per cent. of magnesia (MgO).

$$\text{Log } 36.243 = 1.5592241.$$

Then, as 1 gramme was taken for the estimation, the weight of $\text{Mg}_2\text{P}_2\text{O}_7 \times 36.243 =$ percentage of MgO .

$0.0076 \times 36.243 = 0.275 \div 0.28 =$ percentage of magnesia in the sample of limestone.

SUMMARY OF RESULTS.—Raw limestone.

	Per cent.
Volatile matter,	43·21
Silica,	0·63
Alumina,	0·51
Lime,	55·46
Magnesia,	0·28
Sulphur, &c. (not estimated),
	<hr/>
	100·09
	<hr/>

ANALYSIS OF CALCINED LIMESTONE.

Proceed as in the analysis of limestone, but for the estimation of volatile matter use 10 grammes of the sample. For precipitating the lime, use 60 c.c. of ammonium oxalate solution (see p. 163), and for precipitating the magnesia use 4 c.c. of 20 per cent. ammonium phosphate solution.

ANALYSIS OF DOLOMITE.

Outline of the Process.—With the exception of the modifications required on account of the higher percentage of magnesia in dolomite, the method of analysis is the same as detailed for limestone in the preceding pages.

Estimation of Volatile Matter.—Proceed as directed for limestone on pp. 98 to 100, but, as the volatile matter is sometimes more difficult to drive off, continue the heating for a longer period.

Estimation of Insoluble Matter.—Proceed as directed for limestone on pp. 101 and 102.

Estimation of Alumina and Oxide of Iron.—Proceed exactly as directed on pp. 103 and 104.

Estimation of Lime.—Proceed as directed on pp. 105 and 106, except that, before precipitating the lime, add a strong solution of about 6 grammes of ammonium chloride. This prevents the precipitation of magnesia when oxalate is added, and, further, it checks the solvent action of magnesium chloride on calcium oxalate.

Estimation of Magnesia.—Proceed as directed for limestone estimation, but use 15 c.c. of the 20 per cent. ammonium phosphate solution (see p. 164).

PROXIMATE ANALYSIS OF SOLID FUELS—
COAL, COKE, &c.

Particular attention should be paid to the mechanical condition of the fuel. For the estimation of ash and of moisture the sample operated on should be very finely powdered. If the sample supplied is not finely powdered, a portion of the sample should be carefully selected, and the whole of the selected portion crushed fine enough. From the finely powdered sample the necessary quantities should be accurately weighed off.

The estimations required are—

- (a) Estimation of moisture.
- (b) Estimation of ash.
- (c) Estimation of coke.
- (d) Calculations of the percentage of fixed carbon ; and also
- (e) An abstract of results.

(a) ESTIMATION OF MOISTURE.

Select a flat porcelain basin of about 7 cm. (or $2\frac{3}{4}$ inches) diameter, wipe it dry, weigh, and note the weight.

The basin may be dried by heating it over the flame of a Bunsen burner (care being taken not to crack the basin) for 5 or 10 minutes, and allowing it to cool in a desiccator.

Weigh into the basin 2 grammes of the finely powdered sample.

Set the basin and contents in a steam oven at

about 100° C., and allow to remain there for 1½ hours.*

Take the basin and contents from the steam bath, and allow to cool in a charged desiccator. (Continue to keep the steam bath up to 100° C.)

When cool, weigh, and note the weight.

Set the basin and contents back in the hot steam oven; allow to remain for about 15 minutes or more, withdraw, and replace in the desiccator, and, when cool, reweigh and note the weight found.

If necessary, repeat the heating, cooling and weighing.

EXAMPLE —

Before drying —

	Grammes.
Weight of basin + sample	= 19·4375

Weight of basin only	= 17·4375
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Weight of sample	= 2·0000
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Weight of basin + sample before drying	= 19·4375
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Weight of basin + sample after drying	= 19·3533
---------------------------------------	-----------

	<u>0·0842</u>
--	---------------

$$\frac{0·0842 \times 100}{2} = 0·0842 \times 50 = 4·21.$$

4·21 = percentage of moisture in the sample.

NOTE.—Time permitting, the dried sample may be used for the estimation of ash, by

* Some, if not all, samples of coal when heated too long gain in weight, owing, it is supposed, to the oxidation of sulphur in the sample. The writer found that the maximum loss of weight from a large number of coals was obtained on heating for 1½ hours.

cautiously burning off all combustible matter (in a muffle), allowing to cool in a desiccator, weighing and calculating.

(b) ESTIMATION OF ASH.

Either use the dried sample—from the estimation of moisture—or

Select a round bottomed porcelain basin about 7 cm. (or $2\frac{3}{4}$ inches) diameter, wipe it dry, weigh and note the weight.

Weigh into the basin 2 grammes of the finely pounded sample.

Place the basin and sample in front of a hot muffle, and, after a little time, push the basin and contents further in, and, after a little more time, place them in the hottest part of the muffle.

Allow to remain until all the combustible components have burned off.

Withdraw the basin to the sole in front of the muffle.

When partly cooled place in a charged desiccator, and, when fully cooled, weigh.

EXAMPLE —

	Grammes.
Weight of basin + ash	= 17.5622
Weight of basin only	= 17.4375
	<hr/>
	0.1247
	<hr/>

$$\frac{0.1247 \times 100}{2} = 0.1247 \times 50 = 6.235.$$

6.24 \div percentage of ash in the sample.

(c) ESTIMATION OF COKE OBTAINABLE FROM COAL.

Dry a No. 2 porcelain crucible and lid.

Weigh the crucible and lid, and note the weight.

Weigh into the crucible 10 grammes of the powdered sample, taking care to see that the lid is kept on the balance pan while weighing off the sample.

Place the lid on the crucible.

Place the whole in a warm part of a hot muffle.

In a short time a flame should appear between the crucible and the rim of the lid.

Keep the crucible, with the lid on, in the muffle as long as the flame can be seen.

Withdraw the crucible, &c., to the sole in front of the muffle.

Allow to remain there until partly cooled.

Place in a charged desiccator, and, when fully cooled, weigh.

EXAMPLE—

Before coking—	Grammes.
Weight of crucible and lid + sample	= 40.5362
Weight of crucible and lid	= 30.5362
Weight of sample taken	= 10.0000
After coking—	
Weight of crucible + lid + coke	= 37.2713
Weight of crucible and lid only	= 30.5362
	<u>6.7351</u>

$$\frac{6.7351 \times 100}{10} = 6.7351 \times 10 = 67.35.$$

67.35 = percentage of coke.

(d) CALCULATION OF PERCENTAGE OF FIXED CARBON.

	Grammes.
Percentage of coke as found by experiment	= 67.351
Percentage of ash as found by experiment	= 6.235
	<hr/>
	61.116
	<hr/> <hr/>

61.116 = percentage of fixed carbon.

(e) ABSTRACT OF RESULTS.

	Grammes.
Fixed carbons	= 61.12
Volatile carbon (hydrocarbons, &c.)*	= 28.43
Ash	= 6.24
Moisture	= 4.21
	<hr/>
Total	= 100.00
	<hr/> <hr/>

ESTIMATION OF SULPHUR IN COAL OR COKE.

Weigh off 9 grammes of partly slaked lime which is as free as possible from sulphur and silica. (The amount of sulphur in the lime must be estimated and deducted.)

Place about half of it in a 7 cm. (about $2\frac{3}{4}$ inches) round bottomed porcelain basin.

Weigh off (accurately) 3 grammes of the carefully selected and finely-powdered sample of coal or coke.

Transfer the weighed sample to the basin.

* By difference.

Stir so as to mix the lime and the weighed sample thoroughly.

Spread the remainder of the weighed lime over the mixture, so as to form a covering.

Place the basin and contents in a hot muffle.

Allow to remain for at least 45 minutes.

Draw the basin to the front of the muffle, and stir up the contents so as to expose any unburnt portions.

Replace in hot part of the muffle.

Allow to remain for 10 minutes or more.

Stir up the contents again, and search for unburnt coal or coke.

If the carbon has all been burned off, place the basin in a safe place to cool a little.

Transfer the contents to a 13.5×8 cm. (about $5\frac{1}{2}$ inches \times $3\frac{1}{4}$ inches) beaker.

Add about 50 c.c. of water.

Add about 2 c.c. of bromine and stir well.

Add a sufficient quantity of strong hydrochloric acid to dissolve the lime, &c.—about 33 c.c. should be sufficient.

Boil briskly for at least five minutes.

Filter, collecting the filtrate (and washings) in a clean 6-inch \times $3\frac{3}{4}$ -inch beaker.

Wash well with hot water.

Heat the filtrate and washings just to boiling point.

Add 10 c.c. of warm 10 per cent. barium chloride solution.*

* The barium chloride presented is capable of precipitating 0.131 gramme of sulphur = 0.952 gramme of BaSO_4 = 4.57 per cent. of sulphur from the coal or coke: a plentiful excess.

Place a clock glass on the beaker.

Boil briskly for about seven minutes

Allow the precipitate to settle.

Wash three times by decantation through a 9 cm. Swedish filter.

Wash the precipitate on to the filter.

Wash about ten times with hot water.

Test the washings for the presence of chlorine.

If necessary, continue the washing.

Dry the filter paper and precipitate.

Ignite in a tared No. 0 porcelain crucible for about thirty minutes in a hot muffle.

Allow to cool in a desiccator.

Weigh, and calculate the result.

EXAMPLE—

	Grammes.
Weight of crucible + precipitate + ash	= 7.1343
Weight of crucible	= 7.1263
	<hr/>
Weight of precipitate + ash	= 0.1911
Weight of ash + BaSO ₄ due to sulphur in the lime used	= 0.0041
	<hr/>
Weight of BaSO ₄ due to sulphur in the sample	= 0.1870
	<hr/>

$$\frac{0.187 \times 32 \times 100}{233 \times 3} = 0.187 \times 4.587 = 0.856.$$

0.856 = percentage of sulphur in the sample.

ESTIMATION OF IRON.

VOLUMETRIC METHODS.

Frequently the amount of iron in a substance may be conveniently and accurately ascertained by a volumetric method. For this purpose the sample must be brought into solution under proper conditions. Standard solution of an oxidising agent is then added from a measuring apparatus, and, when the oxidation is complete, the measured volume of the standard solution is noted and the necessary calculations are made.

Towards the end of a reaction the standard solution is cautiously added drop by drop, and as the strength or power of the standard solutions are known, such volumetric estimations are known as titrations—from a French word, *titre*, signifying power or capacity.

The methods generally employed in the volumetric estimation of iron are :—

- (a) Marguerite's—the Permanganate method—
and
- (b) Penny's—the Dichrome method.

Both methods are based on the amount of oxidising agent required to convert ferrous salt to ferric salt.

The dichrome method is generally preferred in British iron works.

In each case a weighed portion of the sample is dissolved in acid. If all the iron is not in the ferrous state it must be reduced—unless it is intended to estimate, separately, the ferrous and ferric iron—and any excess of reducing agent driven off or “corrected.” The solution (reduced if necessary) is subjected to the selective, oxidising action of a standardised solution carefully measured from a burette. When the ferrous iron has all been oxidised, the quantity of standard solution used is read off and the necessary calculations made.

The state in which the iron exists in a solution is shown by indicators, thus—

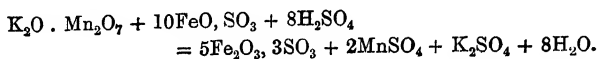
A drop of acidified ferrous solution, when brought into contact with a drop of weak solution of ferricyanide (not ferrocyanide) of potash, yields a blue colouration or a blue precipitate.

A drop of acidified ferric solution, when brought into contact with a drop of alkaline sulpho-cyanide (thiocyanate of ammonia, potash, or soda) solution, shows a blood-red colour, or, if in very small quantity, a faint pink colour.

Convenient reducing agents are nascent hydrogen (from action of acid on zinc); sulphurous anhydride; and, for dichrome titration, stannous chloride.

ESTIMATION OF IRON BY TITRATING WITH A STANDARD
SOLUTION OF POTASSIUM PERMANGANATE
($K_2O \cdot Mn_2O_7$).

The reaction which takes place on peroxidising ferrous iron may be represented thus:—



When all the iron has been oxidised to the ferric state further additions of potassium permanganate impart a pink colour to the liquid in the flask.

Quantity of potassium permanganate required for standard solution for the estimation of iron.

The molecular weight of potassium permanganate is 316.3.

316.3 grammes can peroxidise 55.9×10 grammes of ferrous iron, and

$$\frac{316.3}{559} = 0.56583.$$

or every gramme of iron requires 0.56583 gramme of permanganate.

If, therefore, 5.6583 grammes of potassium permanganate are dissolved and made up with water (at $15.5^\circ C.$) to 1 litre, every c.c. of the solution will equal 0.01 gramme of iron.

PREPARATION OF STANDARD SOLUTION OF PERMANGANATE FOR THE ESTIMATION OF IRON.

Pound in a mortar about 2 grammes of pure potassium permanganate. This will be a sufficient quantity for a student to experiment on.

Dry the pounded sample.

Weigh off 1.415 gramme of the salt. (The theoretical quantity required is 1.4146 gramme.)

Transfer the weighed quantity to a 400 c.c. beaker or beaker flask.

Add about 100 c.c. of warm distilled water.

With a glass rod (without rubber) stir well to hasten solution.

Pour some of the liquid into a 250 c.c. glass-stoppered graduated flask, taking care not to allow any undissolved salt to enter the flask.

Add more warm distilled water to the contents of the beaker.

Stir well, as before.

Pour off more of the solution into the flask.

Make sure that all the salt is dissolved.

Transfer the remainder of the solution to the graduated flask.

Make up nearly to the mark with cold water.

Bring the solution to 15.5° C. and make up to the mark with water at that temperature.

Stopper the flask and shake it briskly.

NOTE.—Once a standard solution is made up it must be kept carefully stoppered. If a quantity of standard

solution is made for stock, the containing bottle should have a label showing the strength of the solution and the date of standardising. Portions of the standard solution which have been taken out must not be returned to the bottle.

PREPARATION OF A SAMPLE OF MOHR'S SALT
FOR STANDARDISING.

Mohr's salt is a compound sulphate of iron and ammonium $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and, when pure, contains 14.26 per cent., or nearly one-seventh its weight of ferrous iron. It may be purchased "chemically pure," or be prepared in the laboratory by the following method:—

Weigh off 27.8 grammes of pure recrystallised ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

Dissolve in minimum quantity of water at 40° C.

Weigh off 13.2 grammes of pure ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$.

Dissolve in minimum quantity of cold water.

Pour the ammonium sulphate solution into the solution of ferrous sulphate.

A granular precipitate of the double sulphate forms as the solution cools.

Wash by decantation.

Dry between the folds of bibulous paper under a press.

Preserve the dried sample in a clean, dry, stoppered bottle.

ARTICLES REQUIRED FOR STANDARDISING THE
PERMANGANATE SOLUTION.

These articles should all be ready before beginning to standardise.

A 30 or 50 c.c. burette, graduated in one-tenths; burettes for permanganate solution must have glass stopcocks.

An Erdmann's float.

A burette stand.

Three clean, dry, 10-oz. conical or globular flasks.

The standard solution, and

About 10 grammes of pure, dry Mohr's salt
or a few grammes of pure iron wire.

STANDARDISING THE PERMANGANATE SOLUTION
BY MOHR'S SALT.

Clean the burette, first with water and then with some of the standard permanganate solution.

Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with standard permanganate solution.

Put in the Erdmann's float and adjust to zero.

Weigh off accurately about 1.75 grammes of the Mohr's salt, and note the weight taken.

Transfer to a clean, dry 300 c.c. (about 10-oz.) conical or globular flask.

Add 100 c.c. of distilled water, to which about

5 c.c. of pure sulphuric acid has previously been added.

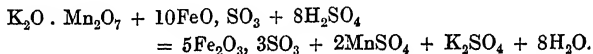
Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile or piece of white paper when examining for the colour.

Continue to add standard permanganate solution cautiously, and with occasional shaking of the flask, until a faint permanent pink colour appears.

The reaction may be expressed by the equation—



Read off and note the quantity of standard permanganate solution required to complete the reaction.

A little quantity of the permanganate solution is required to impart a pink tint to the solution in which the salt was dissolved. To allow for this a blank experiment should be made thus:—

Into a 300 c.c. (about 10-oz.) conical flask measure 100 c.c. of distilled water and 6 c.c. of pure sulphuric acid.

Note the amount of standard solution in the burette, and from it run two or three drops into the conical flask.

Shake the flask so as to mix the contents.

Compare the pink tint with that in the flask in which the iron estimation has just been made.

If necessary, add more standard permanganate to bring the liquid to the same depth of colour.

Note the quantity taken, and deduct from the amount noted as required to effect the oxidation of the iron solution.

Calculate the result.

EXAMPLE OF CALCULATION—

1.776 gramme of Mohr's salt required 25.30 c.c. of the standard permanganate solution, after making allowance for the blank colouration.

$$\text{Iron in Mohr's salt, } \frac{1.776 \times 14.26}{100} = 0.2533,$$

$$\frac{0.2533}{25.30} = 0.010012.$$

Every 1 c.c. of the standard permanganate solution = 0.010012 gramme of iron.

Experiments on 2.035 grammes and on 1.638 grammes, together with the result recorded above, showed that (on an average) every c.c. of the standard permanganate solution = 0.010011 gramme of iron.

EXERCISES IN THE ESTIMATION OF IRON BY MEANS OF STANDARD PERMANGANATE SOLUTION.

Clean a burette with distilled water and then with standard permanganate solution. Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution, put in an Erdmann's float, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a clean, dry 300 c.c. (about 10-oz) conical or globular flask.

Add about 100 c.c. of water to which about 5 c.c. of sulphuric acid has been added.

Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile, or a piece of white paper, when examining for colour.

Continue to add the standard permanganate solution cautiously, and with occasional shaking, until a faint pink colour is obtained which is permanent even after shaking the flask.

Read off, and note the quantity of standard solution required to complete the reaction.

Deduct the quantity required for blank.

Calculate the result.

EXAMPLE—

Weight of Mohr's salt taken = 2.0092 grammes.
Standard permanganate solution required, less the quantity for blank = 28.61 c.c.

Every c.c. = 0.010011 gramme of iron.

$28.61 \times 0.010011 = 0.2864$ gramme.

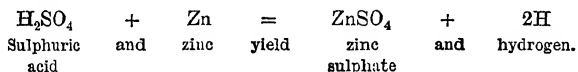
$0.2864 =$ weight of iron found in 2.0092 grammes of Mohr's salt.

$$\frac{0.2864 \times 100}{2.0092} = 14.254$$

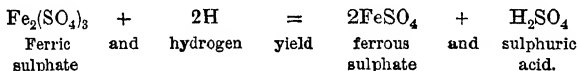
and 14.254 = percentage of iron found in Mohr's salt.

Having—by means of standard permanganate solution—oxidised the iron to the ferric state, the iron in the solution should now be *reduced* to the ferrous condition.

Reduction of ferric solutions may be effected by means of a reductor (see p. 160) or by adding granulated zinc, or small pieces of thin stick zinc and sulphuric acid. The zinc used for this purpose should be free from iron. The reaction between the zinc and acid gives rise to the evolution of hydrogen:—



The zinc sulphate remains in solution, and takes no part in the work; the ferric salts are reduced to ferrous by the action of nascent hydrogen, thus:—

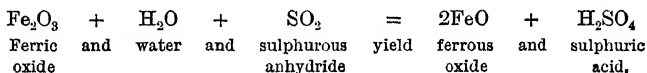


To ascertain if all the ferric iron has been reduced, bring a drop of the solution on the end of a stirring rod into contact with a drop of dilute thio-cyanate (sulphocyanide) solution on a white enamelled slab or a piece of drop-reaction paper. If more than a faint pink colour results, reduction is not complete.

Prof. M. M. Pattison Muir points out (*Chemical News*, 31st January, 1908) that if a small quantity of zinc is used for effecting reduction the action is slow, and if a large quantity of zinc is used time is lost in completing its solution. He suggests the addition of

saturated aqueous solution of mercuric chloride as soon as the reduction is finished. This stops the further action of acid on the remaining zinc, and allows the titration to be proceeded with at once. The author now uses mercuric sulphate in dilute sulphuric acid to stop the action of acid on the zinc. This he prefers to the usual practice of filtering through glass wool.

Sulphurous anhydride, as supplied in syphons, is very convenient for reducing ferric solutions. Water strongly charged with the gas is poured into the solution, and a reaction takes place which may be represented by the equation—



If sulphurous anhydride is used as the reducing agent, excess must be boiled off.

When the solution has been brought into proper condition, proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again, and repeat the titration.

ESTIMATION OF IRON IN ORE BY MEANS OF STANDARD PERMANGANATE SOLUTION.

Before making an assay by titration, the student should practise the exercises set on the previous pages.

Collect the articles required (see p. 123).

Clean the burette, first with water, and then with some of the standard permanganate solution. Run

off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution. This solution should, after two or three weeks, be restandardised before using.

Place an Erdmann's float in the solution in the burette.

Adjust the float to zero.

The ore, having been carefully sampled, and the sample pounded, well mixed, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Place the weighed portion in a 300 c.c. (about 10 ozs) conical flask.

Add about 100 c.c. of dilute sulphuric acid (6 vols. of acid to 100 of water).

Put a funnel in the neck of the flask, and set on a hot plate so as to hasten solution.

When all the iron has dissolved, remove the flask, wash the condensed liquid on the funnel into the flask, and reduce the ferric oxide as directed on p. 127.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken, and deduct the blank

Calculate the percentage (see example on p. 126).

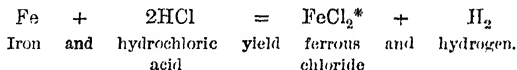
If ferrous and ferric oxides are required, proceed as directed on p. 139.

ESTIMATION OF IRON BY TITRATING WITH A STANDARD SOLUTION OF POTASSIUM DICHROMATE ($K_2Cr_2O_7$ or $K_2O \cdot 2CrO_3$).

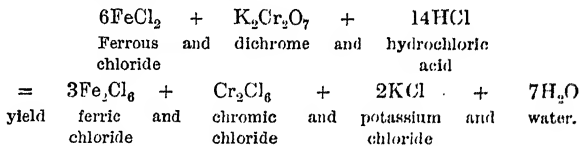
This orange - coloured salt (commonly called "bichrome") can be readily obtained in a fair state of purity, and its solution, if properly kept, remains constant in strength for a long time : it is practically permanent. Under easily-established conditions it parts with oxygen to ferrous oxide (FeO), converting it into ferric oxide (Fe_2O_3).

By measuring the amount of standardised dichrome solution required to effect the change, the amount of iron which was present in the ferrous state can be ascertained.

The chemical changes which take place when iron is dissolved in hydrochloric acid may be expressed by the following equation :—



On adding dichrome solution the ferrous chloride is acted on, and the chemical reactions which occur may be indicated thus :—



* Unless precautions are taken, the ferrous solution soon becomes more or less completely converted into ferric solution having a yellow colour.

This equation shows that 1 gramme of iron requires 0·878 gramme of dichrome to complete the reaction.

TO PREPARE A STANDARD SOLUTION FOR THE ESTIMATION OF IRON.

Weigh off 17·6 grammes of pure, dry dichrome. This quantity is, in practice, more convenient than the theoretical amount—17·56 grammes.

Transfer to a graduated litre flask.

Dissolve the salt in about 600 c.c. of distilled water, and, when the solution is at 15·5° C., make up to the mark with distilled water at that temperature.

Pour, if necessary through a dry filter, into a Winchester quart bottle.

Measure another litre of water in the graduated flask, and pour or filter it into the Winchester.

Mix the solution thoroughly.

TO STANDARDISE THE DICHROME SOLUTION.

Collect the following solutions and articles on the working bench :—

The prepared dichrome solution.

A dilute solution of stannous chloride (see p. 171) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferri-cyanide. This must not be confounded with

the more common ferrocyanide. About 0.1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs about 10 c.m. (or 4 inches) square.

Stirring rods for the ferricyanide and the thiocyanate solutions.

A porcelain basin about 7 inches diameter.

A glass rod about 8 inches long.

A reagent bottle containing pure re-distilled hydrochloric acid.

A wash-bottle containing hot water.

A burette stand, and

A burette, graduated in one-tenths.

Iron wire, pure by preference, or pure, dry ferrous ammonium sulphate or Mohr's salt (see composition on p. 122).

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the dichrome solution, and adjust to zero.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Weigh off accurately about 2 grammes of Mohr's salt, note the weight taken, and transfer to the porcelain basin.

Add about 150 c.c. of distilled water, and about 50 c.c. of hot water.

Add about 20 c.c. of pure re-distilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of dichrome solution required to complete the reaction.

Calculate as in the following example:—

2.0336 grammes of Mohr's salt, which contains 14.26 per cent. of iron, required 28.85 c.c. of the dichrome solution.

Iron in weighed quantity of Mohr's salt

$$= \frac{2.0336 \times 14.26}{100} = 0.28999 \text{ gramme.}$$

Value of the dichrome solution

$$\frac{0.28999}{28.85} = 0.01005.$$

∴ Every 1 c.c. of the standard dichrome solution = 0.01005 gramme of iron.

Make one or two additional estimations, and if all nearly agree, the mean may be taken. The winchester may then be labelled so as to show the strength of the solution and the date of standardising.

EXERCISES IN THE ESTIMATION OF IRON BY MEANS OF STANDARD DICHROME SOLUTION.

Collect the solutions and articles mentioned on pp. 131 and 132.

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the standard solution, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a 7-inch porcelain basin.

Add about 150 c.c. of distilled water, 50 c.c. of hot water, and 20 c.c. of pure, redistilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

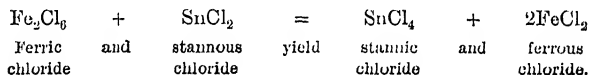
Note the quantity of solution required to complete the reaction.

Calculate as shown in the example on p. 126.

Having, by means of the dichrome solution, oxidised the iron to the ferric state, the iron in the solution should now be reduced to the ferrous condition.

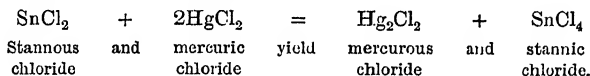
Solutions containing ferric iron are reduced by the addition of acid solution of stannous chloride ($SnCl_2$), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus:—



To find the exact point at which the reduction to ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

To guard against presence of excess of stannous chloride (which excess would spoil the accuracy of the estimation), about 4 c.c. of a 5 per cent. solution of mercuric chloride is added to the iron solution which has just been reduced. Excess of stannous chloride, if present, forms a white precipitate when the mercuric chloride is added. The following equation represents the change:—



The ferrous solution will then be ready for re-titrating with standard dichrome solution.

Proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again and repeat the titration.

A brief recapitulation may now be useful.

Ferric solutions are yellow-coloured; ferrous solutions are colourless.

Ferric solutions yield a blood-red colour when mixed with solution of ammonium thiocyanate (sulphocyanide); ferrous solutions do not.

Ferrous solutions form a blue precipitate or show a blue colour when mixed with potassium ferricyanide solution; ferric solutions do not.

Stannous chloride reduces ferric solutions to ferrous.

Mercuric chloride precipitates and corrects excess of stannous chloride.

Dichrome oxidises ferrous iron in solution to the ferric state, and is unaffected by presence of manganese or other salts usually present in solutions from iron ores, &c.

With a little practice the *rationale* of the method should become clear, and the points at which oxidation and reduction are completed may be determined with accuracy. The experiments should be carefully worked through by the student.

ESTIMATION OF IRON IN ORE BY MEANS OF STANDARD DICHROME SOLUTION.

Before making an assay by titration, the student should practice the exercises set on the previous pages.

Collect the solutions and articles required (see pp 131 and 132).

Clean the burette, first with water, and then with some of the standard dichrome solution, and fix it on the stand.

Nearly fill the burette with the dichrome solution and adjust to zero.

The ore, having been carefully sampled, and the sample pounded, mixed well, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely-pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Transfer it to a 10-oz. conical flask.

Add about 10 c.c. of pure re-distilled hydrochloric acid.

Place a 2-inch funnel in the neck of the flask, and set the whole on a hot plate so as to hasten solution. Solution may be further facilitated by the addition of stannous chloride in re-distilled hydrochloric acid, care being taken to avoid addition of excess.

When all the iron has dissolved, remove the flask, wash the condensed liquid from the funnel and also the contents of the flask into a 7-inch porcelain basin.

Reduce as directed on pp. 135 and 136.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken.

Calculate the percentage.

EXAMPLE OF CALCULATION.

1 gramme of red hematite ore taken for the estimation.

54.6 c.c. of the standard dichrome solution were

required to complete the oxidation of the iron. Each c.c. of the standard dichrome solution was capable of oxidising 0.01002 gramme of iron.

$$\frac{54.6 \times 0.01002 \times 100}{1} = 54.6 \times 1.002.$$

$$54.6 \times 1.002 = 54.71.$$

54.71 = percentage of iron in the sample of ore.

$$54.71 \times \frac{10}{7} = 78.16.$$

78.16 = percentage of ferric oxide (Fe_2O_3) in the sample.

ESTIMATION OF FERROUS AND FERRIC OXIDES IN AN ORE.

Collect the following solutions and articles on the working bench:—

Standardised dichrome solution (see pp. 131 to 134).

A dilute solution of stannous chloride (see p. 416) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferricyanide. This must not be confounded with the more common ferrocyanide. About 0.1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs.

Stirring rods for the ferricyanide and the thiocyanate solutions.

- A porcelain basin about 7 inches diameter.
- A glass rod about 8 inches long.
- A reagent bottle containing pure, redistilled hydrochloric acid.
- A wash-bottle containing hot water.
- A burette stand, and
- A burette, graduated in one-tenths.

Select two 175 c.c. (about 6 ozs.) conical flasks. Fit one with a tight-fitting one-hole rubber cork, and the other with a two-hole rubber cork, and to these fit a doubly-bent glass tube, all as shown in Fig. 19.

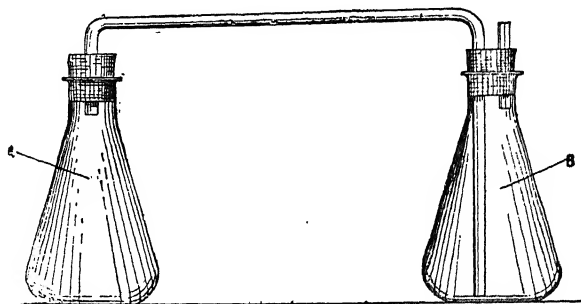


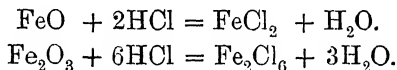
Fig. 19.—Flasks for dissolving iron ore.

Read the general observations on the estimation of iron by means of standard dichrome solution (see p. 131).

For notes on the disintegration of ores, see pp. 251. to 254 of original edition.

Outline of the Process.—On dissolving ore containing ferrous and ferric oxides in hydrochloric

acid, changes take place which may be represented by the equations—



Where, as in this instance, it is intended to estimate ferrous and ferric oxides separately, all apparatus and solutions should be in readiness before beginning to dissolve the ore, so that as soon as the ore is dissolved (as far as practicable), titration may be proceeded with before the solution of the ore appreciably suffers from natural oxidation by exposure to air. Precautions are taken to exclude air while the iron in the ore is being dissolved.

The solution from the weighed portion of the ore is titrated with standard dichrome solution. This effects the conversion of the ferrous compound into ferric. The amount of dichrome solution required is noted and all the ferric and chromic compounds are then reduced by stannous chloride to the ferrous and chromous condition. The solution in the basin is again titrated, and the quantity of standard dichrome solution required for this second titration is a measure of the total amount of iron in the ore. The percentage of ferric iron is estimated by difference. •

Details of the Process.—Measure about 60 c.c. of boiling distilled water into the conical flask (B, Fig. 19).

Dry the other flask, and put about 1 gramme of sodium carbonate into it.

Weigh off 1 gramme of the finely-powdered sample of the ore.

Transfer the weighed portion to the flask containing the carbonate.

Add 10 c.c. of pure re-distilled hydrochloric acid.

At once close the flask with the cork (which should be moistened) to which the glass tube has been fitted.

Press, with a spiral motion, the cork firmly into the neck of the flask.

Dip the other end of the tube into the hot water in the other flask (see Fig. 17).

Apply heat gently until the iron is dissolved.

Remove the apparatus from the source of heat (hot plate or Bunsen burner), and allow the hot water to suck back into the dissolving flask.

Wash the solution; with hot water, into the basin.

Add about 50 c.c. of hot water.

Run in standard dichrome solution while briskly stirring.

Test from time to time by taking a drop from the basin on the end of the stirring rod and dropping on to a "spot" of potassium ferricyanide solution on the white slab or a piece of drop-reaction paper.

Continue the addition of the standard dichrome solution until, on testing, the desired tint is reached.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing

from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

It is essential that this tint should be as near as possible to that at which the operation was stopped when standardising the dichrome.

Read off and note the volume of dichrome solution which has been run in from the burette.

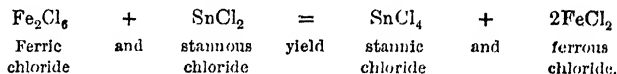
Withdraw the basin, and refill the burette with standard dichrome solution.

Adjust the solution to zero.

Reduce the solution in the basin by adding solution of stannous chloride (see p. 171) while stirring briskly.

Solutions containing ferric iron are reduced by the addition of acid solution of stannous chloride (SnCl_2), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus:—



To find the exact point at which the reduction to

ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

When reduction appears to be nearly completed, test for presence of ferric iron.

If necessary, cautiously drop in more of the stannous chloride solution, stir well, and test again.

Continue to add stannous chloride and to test.

When, on applying the test, only a faint pink colour is developed, add about 4 c.c. of a 5 per cent. solution of mercuric chloride to correct, if necessary, any excess of stannous chloride.

Again test on a thiocyanate spot, and make sure that no ferric iron is present.

Run in from the burette two drops of the standard dichrome solution.

Test on a sulphocyanide spot. The contrast between the colour of this last "spot" and the previous one should be quite apparent if all has been properly done.

Complete the titration by the cautious addition of standard dichrome solution.

Note the quantity of standard solution used to complete the oxidation.

Calculate the result.

EXAMPLE OF CALCULATION.

One gramme of sample of clayband ironstone taken for the estimation.

Each c.c. of the standard dichrome solution was capable of oxidising 0.01001 gramme of iron.

29.93 c.c. of the standard dichrome solution were required to oxidise the ferrous iron, and, after reduction, 31.8 c.c. were required to complete the oxidation of the iron.

Ferrous iron—

$$\frac{29.93 \times 0.01001 \times 100}{1} = 29.93 \times 1.001,$$

$$29.93 \times 1.001 = 29.96.$$

29.96 = percentage of ferrous iron.

Total iron—

$$\frac{31.8 \times 0.0100 \times 100}{1} = 31.8 \times 1.001,$$

$$31.8 \times 1.001 = 31.83.$$

31.83 = percentage of total iron.

Then, Total iron, . . . = 31.83 per cent

Ferrous iron, . . . = 29.96 „

Ferrie iron, by difference, = 1.87 „

Ferrous oxide (FeO)—

$$29.96 \times \frac{2}{7} = 38.52,$$

and 38.52 = percentage of ferrous oxide.

Ferric oxide (Fe_2O_3)—

$$1.87 \times \frac{1}{7} = 2.67,$$

and 2.67 = percentage of ferric oxide.

GENERAL NOTES ON LABORATORY OPERATIONS AND APPLIANCES.

Fine-Pounding or Grinding of Samples.—Friable samples are reduced to very fine powder—"impalpable powder"—in an agate mortar with an agate pestle. To facilitate pulverising, the pestle is mounted in a wooden handle with a ferrule, and the mortar is fitted into a recess in a long piece of hard wood. Very small quantities are ground at a time, and they are reduced to the finest state possible by attrition. The finished sample should be absolutely free from gritty particles.

Weighing is conducted on delicate chemical balances. In institutions where balances are used by junior students it is advisable to always test the accuracy of a balance before using.

The amount of sample weighed off for an estimation depends on the percentage of the constituent to be estimated, the process to be followed, the quantity of the finished precipitate, and on other considerations. A sample of steel for the estimation of carbon by colour requires to be weighed off more accurately than a sample of the same steel for the estimation of sulphur. A sample of rich ferromanganese for the estimation of manganese requires to be weighed off with greater accuracy than a sample of steel for the estimation of phosphorus. To illustrate this point: Consider what would be the result of an erroneous overweighing to the

extent of 0.001 gramme in each of the above instances :—

2.001 grammes of steel (containing 0.05 per cent. of phosphorus). Result shown, on the assumption that 2.000 grammes had been weighed out for the estimation, 0.050025 per cent.

0.501 gramme of ferro-manganese (containing 80 per cent. of manganese). Result shown, on the assumption that 0.500 gramme had been weighed out for the estimation, 80.16 per cent.

In weighing out small quantities of rich substances it is better to finish weighing with the rider than to attempt to weigh an exact quantity. This is specially the case in weighing out pure materials for standardising.

Finished precipitates require to be weighed very accurately. In estimating sulphur in steel, for instance, an error of 1 milligramme in the final weighing would cause a serious difference in the percentage returned. Such a wide difference is mentioned here to illustrate: it ought never to occur in practice.

Dissolving.—The weighed sample, in the form of drillings or turnings or in powder of the required fineness, may be dissolved in acid or may require to be fused with a suitable chemical. Iron or steel which cannot be dissolved in strong nitric acid may be dissolved in diluted acid if not too weak.

Sulphuric acid of the usual strength (1.84 specific gravity) is, when diluted, used for dissolving substances which are to be titrated with standard potassium permanganate solution.

Fuming hydrochloric acid—water saturated with gaseous hydrochloric acid—contains 42 per cent. of hydrochloric acid. Its specific gravity is 1.21. As usually sold it is diluted to a specific gravity of 1.16, and it then contains 32.02 per cent. of hydrochloric acid. On prolonged boiling of either of these, acid is driven off till a solution containing 20.2 per cent. of acid is reached. A weaker solution loses water on being boiled. For corresponding notes on nitric acid see p. 409, and on sulphuric acid see p. 416. For dissolving in acids under pressure see p. 253.

Fusing.—The sample is intimately mixed with fusion mixture, potassium bisulphate, sodium peroxide, or Stead's reagent, and heated in a nickel, platinum, or silver basin or crucible till the contents become fused or liquefied. Heating is effected in a muffle furnace, or over a blowpipe or a Mecker burner. The latter is very convenient. The "melt," as the liquefied mass is called, is allowed to cool and is afterwards dissolved.

Evaporating excess acid, taking down to dryness and baking or roasting, is carried on in basins or beakers over a hot plate.

The hot plate used by the author consists of 4 cast-iron plates, each 50.5×22 cm. (about $20 \times 8\frac{3}{4}$ inches), and each having 7 equidistant rows of 35 studs cast on its under side, each stud being 0.5 cm. ($\frac{3}{16}$ inch) deep and 0.5 cm. diameter, and 1.3 cm. apart from each other. A horizontal gas pipe with small burners or jets is laid under each of the plates. The tips of the flames from the

burners envelop the studs, and the plates are heated with a comparatively small consumption of gas. The heat is sufficient to enable the contents of beakers or basins to be evaporated to complete dryness without changing the residues into that condition in which they cannot be dissolved without difficulty. As the plates are 1.3 cm. (about $\frac{1}{2}$ inch) thick they do not warp or buckle.

Beakers or basins containing liquids which are to be evaporated are placed on a directly-heated plate; wash-bottles may be kept warm, or solutions with precipitates may be set to settle, on the adjoining plates without gas-heating. The four plates are set in a frame, and the arrangement, which was first designed for a Staffordshire steel work, was supplied by Messrs. Fletcher, Russell & Co., Warrington, is very useful in a laboratory.

Evaporating to dryness—in order to bring a washed precipitate into condition for weighing—is generally conducted in platinum or porcelain basins on a water bath. The author uses "platinised nickel" basins—basins pressed into shape from compound sheeting composed of two thin platinum sheets hot-rolled with a central sheet of nickel. These were recommended by the late Prof. Dittmar, and are very convenient for rapidly dealing with phospho-molybdate precipitates. The basins are made with ledges for supporting them over suitable-sized openings in the top of the water bath.

Precipitating, Filtering, and Washing.—These are stages in the separating of one constituent from others.

A precipitate is a solid which is almost, but never absolutely, insoluble in the liquid in which it is precipitated. Precipitation should be effected with the view of forming crystals or granules of definite chemical composition capable of being easily separated from the containing liquid when poured on a filter of porous paper and washed. Generally larger crystals or grains are formed in hot liquids than in cold ones. The larger crystals or granules are not so likely to clog the pores of the filter. A more open or porous filter-paper can, therefore, be used, and washing can be done more quickly. On adding cold ammonium oxalate solution to cold calcium chloride solution, an unsatisfactory precipitate (for washing) is formed. If one of the solutions is hot, a better precipitate appears; if both solutions are at the boiling point a still more satisfactory precipitate is obtained. And if, after the addition of the hot precipitant to the hot calcium chloride solution, the liquid containing the precipitate is boiled, a precipitate is found which settles rapidly, and can be quickly washed with satisfactory results.

In some instances, as in the precipitation of magnesium-ammonium-phosphate, the precipitate should be added drop by drop, and each addition should be accompanied by violent agitation. On the other hand, ammonium molybdate solution should be added all at once.

Some precipitates rapidly subside, and filtration is facilitated if the beaker or flask is set aside in a slanting position so as to cause the precipitate to settle at the bottom towards the side from which the liquid will be poured into the filter. A light, flocculent

precipitate, such as the basic hydrate obtained in the course of the gravimetric estimation of manganese, should be filtered off at once, and quickly washed. The gelatinous precipitate of aluminium hydrate should be quickly washed with hot water, and if, through neglect, it happens to become set, further washing is slow and troublesome.

By saturating the filter with hot water immediately before filtering the operation is considerably facilitated.

Washing aims at the removal from the precipitate of the adhering portion of the liquid in which precipitation was effected and of substances dissolved in it. The washing liquid should be of such a nature as not to dissolve more than the unavoidable minimum of the precipitate. A reasonable quantity of the washing liquid should be used, and allowed to drain off before repeating the washing with another like quantity.

The filter should be smaller than the funnel, and the former should not be more than two-thirds full at any time. The washing liquid, ejected from a wash-bottle, should stir up or plough into the precipitate. The filtrate and washings should not be allowed to splash in the collecting beaker.

The filtrate and washings may in some cases be tested (*a*) to ascertain if sufficient precipitant has been used, and (*b*) to ascertain if the precipitate has been sufficiently washed. If the filtrate is not required (*a*) may be ascertained by collecting some of the filtrate in a test-tube and adding a clear solution of some of the substance to be precipitated. Presence of a precipitate in the test-tube is sufficient evidence. To apply test

for (b) some of the latter washings may be allowed to drop into a test-tube and a clear solution containing a substance which can cause a precipitate added. Thus, to test if a magnesium-ammonium-phosphate precipitate has been washed enough, a clear acidified solution of silver nitrate is added to some of the last washings collected in a test-tube. If the collected washings contained chlorides a white precipitate of silver chloride will form. Absence of a precipitate is good evidence of thorough washing, but, to be quite safe, it is advisable to wash two or three times more.

When the filtrate is required for further analysis, no portion can be permitted to be withdrawn for testing. But if the power of the measured quantity of precipitating solution is known, and is compared with the weight of the precipitate, a safe inference may be drawn.

When precipitation is properly carried on—with due regard to conditions—filtering and washing may, in most instances, be quickly and efficiently effected in ordinary filters of good filter-paper. Many contrivances are in use for facilitating filtering—such as filter pumps, bell jars and suction pumps, Gooch crucibles (crucibles with bottoms having numerous small perforations) for working with pumps, and asbestos or pulp filters.

Asbestos filters are prepared by igniting fine-fibred asbestos, allowing to cool, placing in a clean mortar along with water, rubbing with a pestle till the fibres are bruised and broken, pouring the pulp produced

into a Gooch crucible, draining till dry (the filter pump being used), and repeating the washing and draining till no more fibres are washed through. For some purposes asbestos washed with acid may be used instead.

Regarding pulp filters, the following notes contributed by Ibbotson to "Technics" give full practical details for preparing and using them as recommended by Horace Jervis (*Chemical News*, 78, p. 257):—

"Ashless filter-paper clippings are torn into small pieces and vigorously shaken in a bottle with considerably more distilled water than they can absorb. In less than five minutes a filtering medium of fine texture is thus obtained. A porcelain filter plate, $\frac{7}{8}$ inch in diameter, and pierced with about twenty holes each nearly $\frac{1}{16}$ inch in diameter, is placed in the throat of a *smooth* funnel of $3\frac{1}{4}$ inches diameter. Closing the stem of the funnel with the thumb of the left hand, water is then poured on in sufficient quantity to fill the stem and cover the plate, care being taken that no air is imprisoned below the latter. Sufficient pulp is then poured on to give a thickness of felting, for ordinary purposes, of no more than a $\frac{1}{4}$ inch; and having adjusted the plate in a horizontal position by means of a glass rod, the thumb is removed and the water allowed to run away, whilst a rotary motion is imparted to the funnel. By means of a spatula or pair of weight pincers, the felting is then pressed slightly and the edge tucked in, so as to prevent a rise of the pulp when liquids are poured on.

"The funnel may then be arranged for suction;

sufficient pressure may easily be induced by the mouth without resorting to the use of a filter pump.

"A precipitate is effectively and rapidly washed by filling up the funnel twice, and after sucking the water from the stem of the funnel, which is full of liquid throughout the filtration, it only remains to transfer the precipitate (which has been rendered sufficiently dry by the suction) to the ignition dish or crucible. This operation does not at first commend itself to the manipulator. By means of a pair of weight-pincers the edge of the pulp is lifted at any point, and the felting folded over about a horizontal diameter, so as to bring the under surface uppermost. This surface is then grasped by the pincers and the whole filter bodily transferred, precipitate side underneath, to the ignition dish, in which a dry piece of ashless paper has been previously placed. The precipitate, which is still moist, does not therefore make actual contact with the platinum. It now only remains to transfer the small amount of precipitate clinging to the sides of the funnel above the region previously occupied by the pulp. The funnel is grasped in the left hand, leaving the thumb free to rotate it by pressure applied at the rim, whilst a small piece of wetted ashless filter-paper is tightly pressed (by means of the thumb only of the right hand) against the side of the funnel. By gradually bringing the paper from throat to rim during the rotation it will be found possible in most cases, after a little practice, to remove every trace of adhering precipitate by means of a small piece of paper.

"The total amount of paper to be burnt off in the

event of its being found necessary to use a second piece for cleaning the funnel is considerably less than the reader might think; and no harm can be done by making absolutely certain of the thorough cleansing of the funnel by the use of still more paper.

"Precipitates of the barium sulphate type are effectually retained by using a thicker layer of pulp, but no advantage over ordinary filter-papers can be claimed for pulp when handling gelatinous precipitates of the zinc sulphide type.

"Ignition may be commenced at once, or at any rate, after rapidly drying at the mouth of the muffle; and when completed, the ignited residue may be entirely brushed from the crucible, of which the weight is therefore not required.

"All precipitates which may be safely ignited in contact with the paper—and their number is considerably greater than a perusal of text-books on quantitative analysis would lead one to suppose—may be treated as described. The extinction of the last spark, which generally takes place in the centre of the mass, is a guarantee of complete and thorough ignition."

Ignition of filter-paper in contact with certain precipitates, such as ammonium-magnesium-phosphate, is at times troublesome unless precautions are taken.

The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should

remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes difficult to burn off the paper.

When decomposition has to be effected—as in the conversion of calcium oxalate into calcium oxide, or the conversion of the hydrated manganese peroxide precipitate to tri-manganic tetroxide—prolonged ignition in a muffle furnace at a high temperature is required. By using a Mecker burner with blast, these changes may be completed in a few minutes. Ignited precipitates must be allowed to cool down in desiccators, otherwise they would absorb moisture from the atmosphere.

Comparing Colour-depths.—In American works the colorimetric estimation of carbon in furnace samples and finished steel is facilitated by various contrivances. The test piece is rolled through a set of small rolls, or is hammered to form a bar about 8 inches \times 1 inch \times $\frac{1}{2}$ inch, stamped, and allowed to cool on a firebrick slab. It is then placed in a special machine with a horizontal drill. When the skin has been cleared, drillings fall through a funnel into a removable scooped pan which is set on the beam of a delicate balance. The weighing having been quickly completed, and the weighed drillings transferred to a test tube, the measured quantity of nitric acid is dropped in. The test tube is then placed in a bath containing an aqueous solution of calcium chloride, which is kept at its boiling point (110° C.) by high-pressure steam. When the sample is completely dissolved, the test tube is set in a cold-water

vat to cool. The liquid is then transferred to a graduated Eggertz' comparison tube of about 30 c.c. capacity, the upper part of which is bent to an angle of about 115° , and terminates in a small enlargement or funnel. This style of comparison tube facilitates pouring, and the mixing of the contents by shaking.

In comparing depth of colour, the standard Eggertz' tube and the comparison tube are placed in a box or "camera" in a dark room. The camera is blackened within on four sides. Light from an incandescent burner is admitted through a ground-glass plate screened by blue tissue paper. The ground glass disperses the light, and the blue-coloured paper neutralises the yellow rays of light.

For comparing coloured solutions there are several forms of chromometers. One of the best known in steel works is that devised by Mr. J. E. Stead for use in estimating carbon in steel, and described by him in the *Iron and Steel Journal*, 1883, vol. i., p. 217. It consists of two parallel measuring tubes of similar diameter, each about 23 cm. (9 inches) long. These are mounted on a suitable frame having graduation marks and carrying a white disc near the bottom and a reflector at the top. A connection can be made between one of the tubes and a wide-neck bottle—generally of about 120 c.c. capacity—for the solution of standard steel. A syringe is also connected (see Fig. 9).

In working with the chromometer a quantity of the solution from the steel to be tested is placed in the left-hand measuring tube. On squeezing the

syringe, the standard solution is forced into the other measuring tube to form a column which will show a corresponding depth of colour. The percentage is then calculated (see p. 10).

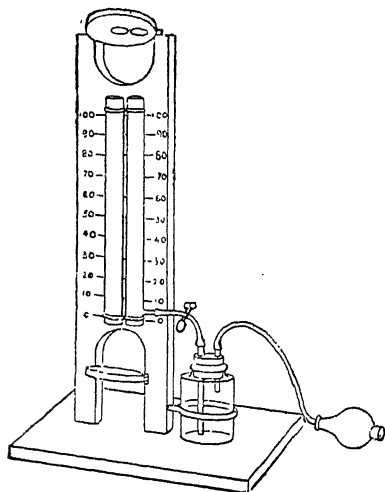


Fig. 9.—Stead's Chromometer.

For volumetric estimations standard solutions and indicators, which readily show a definite "end point," are required. These are fully dealt with in the preceding pages.

For volumetric work, accurately graduated burettes, flasks, &c., may be purchased at very reasonable prices. Pipettes for the estimation of phosphorus in pig iron may be standardised by finding the specific gravity of the solution of pig iron—by means of a 50 c.c. specific gravity bottle—and then finding (by weighing into a

tared beaker) the level in the pipette from which 20.38 c.c. of the solution are delivered. A slip of gummed paper is fastened on the stem, and levels are tentatively marked thereon with pen or pencil. From the result of a few trials the proper level can be easily ascertained. This should be clearly marked with a diamond, or etched with hydrofluoric acid.

The **reductor** mentioned on p. 127 is a glass tube with a stopcock: it is like a wide ungraduated burette. A bulb near the top conveniently increases its capacity.

For use, the reductor is partly filled with pure zinc shot. The ferric solution (containing free acid) to be reduced is poured into the reductor and allowed to remain there till reduction is complete; the tap is then opened, and the solution is allowed to flow out. The remaining zinc is washed with water, the washings being added to the reduced solution. If pieces of zinc have become detached and been carried down with the solution, a little mercuric sulphate (see p. 128) should be added to coat the zinc and prevent further action. Titration may then be proceeded with.

NOTES ON PREPARING AND STORING SOLUTIONS.

Solutions for analytical purposes should be prepared from pure chemicals, and stored in well-stoppered stock bottles (half-Winchesters suit well for many of the solutions) in a store-room screened from direct sunlight and situated in a convenient part of the laboratory.

The shelves should be arranged at suitable distances from each other, and the place for each bottle should be marked by a clearly-printed label carefully covered with paraffin wax. Each stock bottle should have a clearly-printed, wax-covered label. The labels of each row should be arranged on the same level—those for the top row being placed near the bottom of the bottles, those for the bottom row near the top, and those for the intermediate rows placed in intermediate positions, each row differing from the others. Bottles which are thus symmetrically labelled are easily kept in their respective places. If, by mistake, a bottle is placed on a wrong shelf, the error is at once detected, and its proper place is soon found.

Many of the solutions may be conveniently made up in stoneware jugs. These are not so tender as glass ware

Acetic Acid cooled below 15.5° C. forms large, colourless, transparent crystals. Above that temperature these melt and yield a colourless, pungent liquid known as **glacial acetic acid**, which has a density of 1.063. As usually sold, its specific gravity is 1.045, but the strength of this acid cannot with certainty be ascertained by its density. The weight of dry sodium carbonate required to neutralise a measured quantity is a safer guide.

Ammonia liquor, or *liquor ammoniæ*, is a solution of gaseous ammonia in water. The higher the percentage of ammonia in solution the lower its specific gravity. As usually sold it has a specific gravity of 0.88 at 15° C. This saturated solution contains 35 per cent. of ammonia.

Ammonium Acetate.—Neutralise 1.045 specific gravity acetic acid exactly with 0.88 specific gravity ammonia liquor, using phenolphthalein or litmus as indicator.

Ammonium Chloride.—Dissolve 200 grammes of pure ammonium chloride in hot water, and make up with cold water to 1 litre.

Ammonium Molybdate.—Weigh off 50 grammes of pure molybdic acid, stir into 100 c.c. of water, and dissolve in 100 c.c. of 0.88 specific gravity ammonia liquor. Pour the solution into 750 c.c. of cold 1.20 specific gravity nitric acid (see p. 168). Stir

vigorously, or, by means of a foot-bellows, blow air through the dilute nitric acid while adding the other solution. Allow to settle, and, if necessary, filter through a double close-texture filter into the stock bottle.

J. E. Stead uses (see p. 32) a 10 per cent. solution of ammonium molybdate in water. This is used in conjunction with excess of nitric acid.

Ammonium Nitrate.—Dissolve 2 lbs. of pure ammonium nitrate in warm water, filter the solution if necessary, make up with cold water to 1.5 litres, and mix well.

One kilogramme may be similarly treated and made up to 1,650 c.c.

Ammonium Oxalate.—Dissolve 100 grammes of pure ammonium oxalate in $2\frac{1}{2}$ litres of hot water.

Or, dissolve $\frac{1}{4}$ lb. (113 grammes) in $2\frac{3}{4}$ litres of hot water. When cool, make up with water to 2,825 c.c. and mix well.

One c.c. of this solution can cause the precipitation of calcium oxalate equal to 0.0177 gramme of lime.

Ammonium Persulphate.—In order to get a sharp reaction on the addition of this reagent, it is necessary that it should be slightly moistened a few hours before being used. If moistened a day or two beforehand, a sharp reaction may be had. Persulphate may be used instead of bromine in the gravimetric estimation of manganese.

Ammonium Phosphate.—Dissolve 200 grammes of pure ammonium phosphate in 1 litre of warm water. When cool, make up to the 1,000 c.c. mark with cold water and mix well. Or, dissolve $\frac{1}{2}$ lb. (226 grammes) and, when cold, make up with water to 1,130 c.c. and mix well. This solution does not keep well.

One c.c. of this solution can cause the precipitation of ammonium-magnesium-phosphate equal to 0.023 gramme of magnesia.

Ammonium Thiocyanate (Sulphocyanide) for Indicator.—Dissolve 2 grammes of the pure salt in 100 c.c. of water. This solution does not keep well.

Aqua Regia.—Mix 3 volumes of 1.16 specific gravity hydrochloric acid with 1 volume of 1.42 specific gravity nitric acid for use when required.

Barium Chloride.—Dissolve 100 grammes of pure barium chloride in about 300 c.c. of warm water. When cool, make up to 1,000 c.c. with cold water and mix well. 10 c.c. of this solution can cause the formation of a precipitate of BaSO_4 weighing 0.955 gramme.

Cadmium Acetate.—Dissolve 25 grammes of pure cadmium acetate in 500 c.c. of water, add 100 c.c. of glacial acetic acid, and make up with water to 1 litre.

Cadmium Chloride.—Dissolve 40 grammes of pure cadmium chloride in 1 litre of water, add 1 litre of 0.88 specific gravity ammonia liquor and mix well.

Caustic Potash.—See Potassium Hydroxide, p. 169.

Caustic Soda.—See Sodium Hydroxide, p. 170.

Hydrochloric Acid is a colourless gas with a very pungent smell. It is extremely soluble in water. At ordinary temperature and pressure a solution containing 42.9 per cent. of the acid may be obtained. The specific gravity of the saturated solution is 1.212. As usually sold "hydrochloric acid" has a specific gravity of 1.16. When of this density it contains 32.02 per cent. of HCl. Weak aqueous solution of hydrochloric acid loses water when boiled and becomes stronger; a strong solution when boiled loses gas and becomes weaker. In both cases the result is an acid containing 20.24 per cent. of HCl.

Pure hydrochloric acid should be used for analysis.

Hydrochloric Acid of 1.1 Specific Gravity.—To 250 c.c. of 1.16 specific gravity hydrochloric acid add 150 c.c. of water and mix well.

Hydrofluoric Acid.—The aqueous solution of hydrofluoric acid is a corrosive irritating liquid which readily attacks glass vessels. It is, therefore, kept in gutta-percha bottles, which should be kept carefully closed with gutta-percha stoppers. It is seldom sold in a state of purity, and when a few drops are evaporated in a platinum dish (in a fume cupboard, of course) a solid residue is left. The weight should be ascertained and allowed for as a "blank."

Hydrogen Peroxide.—This may be purchased of the required strength, or may be prepared by triturating barium peroxide with water and adding hydrochloric acid and more water. It may also be prepared by acting on sodium peroxide with nitric acid and water.

Iodine Solution for Sulphur Estimation.—Weigh off 2 grammes of re-sublimed iodine and dissolve in 50 c.c. of water containing 4 grammes of potassium iodide. When the iodine has dissolved, make up with water to 1 litre and mix well. Standardise, as directed on pp. 48-51, before using, or if in regular use, re-standardise every third day. If used occasionally, re-standardise before using. Iodine solution should be kept from light in a cool cupboard.

Iron Solution for "Correction" in Gravimetric Estimation of Manganese (p. 38).—Dissolve 0.0177 gramme of fine iron wire (pianoforte wire) in hydrochloric acid, and make up with water to 1 litre.

Magnesia Mixture.—Dissolve 25 grammes of pure magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and 25 grammes of pure ammonium chloride in 400 c.c. of water. Add 200 c.c. of 0.88 specific gravity ammonia liquor and mix well. It is advisable to prepare this solution some time beforehand, and to decant the clear liquid or separate any precipitate which forms by filtration.

One c.c. of this solution may be assumed to be capable of causing the formation of a precipitate of ammonium - magnesium - phosphate containing 0.01 gramme of phosphorus.

Mercuric Chloride.—Dissolve 25 grammes of mercuric chloride in 500 c.c. of warm water.

Methyl Orange for Indicator.—This solution may conveniently be purchased.

Nitric Acid is a colourless, fuming, corrosive liquid, having a specific gravity of 1.53. As usually sold it is diluted with water till its specific gravity is about 1.42. At 1.42 the solution contains 69.34 per cent. of nitric acid.

When strong nitric acid is boiled it is partially

decomposed, nitrogen peroxide and water being formed. When weak nitric acid is boiled, water is driven off. Thus, whether strong or weak, the acid, on being boiled loses either nitric acid or water until the strength reaches 68 per cent. of HNO_3 .

For analytical work pure acid should be used.

Nitric Acid, Dilute, for Carbon Estimation.—Add 200 to 210 c.c. of 1.42 specific gravity nitric acid to 250 c.c. of water and mix well. The specific gravity of the liquid should be about 1.20 when cool. Test with the hydrometer. If required, add either acid or water to correct the density.

Nitric Acid, Dilute, for Volumetric Estimation of Phosphorus.—To 2,500 c.c. of water add 25 c.c. of 1.42 specific gravity nitric acid, and mix thoroughly. The strength of this dilute solution may be ascertained by titrating with standard solution of sodium carbonate. It should also be standardised with the sodium hydroxide solution which is to be used in the phosphorus estimation.

Phenolphthalein for Indicator.—Dissolve 1 gramme of the powder in 300 c.c. of alcohol and add 250 c.c. of water. Add clear, dilute solution of sodium or potassium hydroxide, drop by drop, till the solution becomes pink coloured ; then add dilute nitric acid solution till the colour is just discharged. A prepared solution may conveniently be purchased.

Potassium Dichromate (Dichrome) — Standard Solution for Volumetric Estimation of Iron.—This is prepared and standardised as directed on pp. 131 to 134.

Potassium Ferricyanide for Indicator.—Dissolve about 0.10 or 0.20 gramme of pure potassium ferricyanide in about 100 c.c. of water. Only freshly-prepared ferricyanide solution should be used.

Potassium Hydrate.—See below.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Combustion.—Dissolve 105 grammes of pure potassium hydroxide in water and make up to 250 c.c. with more water. Keep in a bottle with a tight-fitting cork.

Potassium Permanganate—Standard Solution for Volumetric Estimation of Iron.—Prepare and standardise as directed on pp. 121 to 125

Potassium Permanganate for Volumetric Estimation of Phosphorus.—Dissolve 4.264 grammes of potassium permanganate in water, and make up with more water to 1 litre.

Silver Nitrate for Colorometric Estimation of Manganese in Pig Iron.—Dissolve 4 grammes of pure silver nitrate in water, make up to 1 litre with water, and mix well. If, on standing, a precipitate settles out, treat as above. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Colorometric Estimation of Manganese in Steel.—Dissolve 1.33 grammes of pure silver nitrate in water, make up to 1,000 c.c. with water, and mix well. Allow to settle, and, if necessary, filter. If, in consequence of the water not being quite pure, there is more than a slight precipitate, more silver nitrate should be added, and the clear solution filtered off. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Testing Washings.—Dissolve 2 grammes of silver nitrate in 500 c.c. of water, add 500 c.c. of 1.42 specific gravity nitric acid. Allow to stand for a little, and, if necessary, filter. Keep in an amber-coloured bottle or in a dark place.

Sodium Hydrate.—See Sodium Hydroxide below.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Sulphur Estimation.—Dissolve 56 grammes (or 2 ozs.) of pure sodium hydrate in 1 litre of water. Allow to stand for some hours, and, if any sediment has formed, separate the clear portion of the solution by decantation.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Volumetric Estimation of Phosphorus.—(a) Stock solution. Dissolve 68 grammes in water, and, when cold, make up with water to 1,000 c.c. (b) Working solution. Draw off 250 c.c. of the stock solution, make up with water to $2\frac{1}{2}$ litres, and mix thoroughly.

Stannous Chloride (Strong).—To 15 c.c. of water add 30 grammes of pure stannous chloride and stir for a few minutes. Add 450 c.c. of 1.16 specific gravity hydrochloric acid, and heat gently to about 70° C. Continue the stirring to dissolve as much as possible of the salt. If an insoluble residue remains, allow it to settle. Pour off the clear liquid into a suitable bottle. Store in a cool, dark cupboard. On long standing a precipitate of stannic chloride sometimes forms.

Stannous Chloride (Dilute).—Measure off 10 c.c. of the strong stannous chloride solution, make up to 100 c.c. with water, and charge into the dropper for finishing reduction of ferric solutions.

Starch Solution.—Make 1 gramme of potato starch into a thick cream with a little cold water by stirring in an 18 cm. (about 7 inches) diameter porcelain basin. Quickly pour into the cream 500 c.c. of boiling water while stirring vigorously. Boil the solution for two or three minutes, and allow it to cool before using. A starch solution prepared in this manner may remain in good condition for a few days.

Sulphuric Acid is a heavy, oily, colourless liquid, which when strong and pure has a specific gravity of 1.854. When boiled it is decomposed, and gives off sulphur trioxide, as indicated by the equation, $\text{H}_2\text{SO}_4 = \text{SO}_3 + \text{H}_2\text{O}$, until 1.5 per cent. of water is present, after which it distils unchanged.

As usually sold, its specific gravity is 1.84. This strong acid should be cautiously diluted by pouring into water.

Sulphuric acid sold as "pure" sometimes contains lead in solution, which separates on dilution.

Sulphuric Acid, Dilute No. 2 (sp. gr. 1.26), for Dissolving Steel.—Cautiously pour 250 c.c. of 1.84 specific gravity sulphuric acid into 750 c.c. of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphuric Acid, Dilute No. 4, for Use in Sulphur Estimations.—Cautiously pour 100 c.c. of 1.84 specific gravity sulphuric acid to 1 litre of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphurous Anhydride or Sulphurous Acid.—Syphons containing water highly charged with this gas may be purchased. When the charged syphon

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is in an upright position, gaseous anhydride will be delivered on opening the tap. But when the charged syphon is laid horizontally, the anhydride in aqueous solution will be delivered on opening the tap. 5 or 10 per cent. aqueous solutions may also be purchased.

Zinc Chloride.—Dissolve 100 grammes of pure zinc chloride in 1 litre of water.



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TO

A PRACTICAL GUIDE TO IRON AND
STEEL WORKS ANALYSES

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SUPPLEMENT

TO

A PRACTICAL GUIDE TO IRON AND STEEL WORKS ANALYSES.

ANALYSES OF STEELS.

ESTIMATION OF CARBON.

The estimation of carbon by Eggertz' colour test has been fully described in previous pages. The chief recommendation of this method is its convenience. By Eggertz' method it is easy to estimate in a few minutes the percentage of combined carbon in a sample of "metal" drawn from a bath of molten steel, and for guidance in the ordinary routine of steel works' practice the method is of the utmost value.

But for definitely ascertaining the percentage of carbon in treated steels—to find the total carbon (including what is known as "missing carbon"), recourse must be had to the more elaborate and conclusive combustion method.

The combustion method, when systematically carried out, presents little difficulty. When once the apparatus is brought into good working order, the combustion method, with care, regularly yields reliable results.

ESTIMATION OF CARBON BY COMBUSTION.**DIRECT COMBUSTION OF THIN TURNINGS OR
DRILLINGS OF STEEL.**

Outline of the Process.—A weighed quantity of the sample, in the form of turnings or drillings not more than 0.25 mm. thick, is placed in a suitable boat in a porcelain tube set on a combustion furnace. The tube is brought to a bright red heat, and arrangements are made for the delivery of a steady supply of dry, pure air or oxygen. The constituents of the steel are oxidised, and the gases resulting from the oxidation of the carbon are carried forward—care being taken to convert all the carbon into dioxide—and absorbed in a solution of potassium hydrate in a Geissler's or Mohr's absorption bulb. The charged bulb is weighed before and after the combustion. From the increase in weight, due to the carbon dioxide absorbed, the percentage of carbon is calculated.

When oxygen is used the combustion is completed more rapidly than when air is employed. But oxygen is more liable to cause fusion and enclose a little of the carbon. Combustions conducted with air yield a slightly higher result. If precautions are taken to prevent access of moisture and impurities to the solution in the weighed absorption bulb, the higher result may be accepted as more accurate.

Apparatus Required.

(1) A combustion furnace. The kind shown in Fig. 9 is suitable.

This furnace, when made up of four blocks, makes a good support for the combustion tube, but only the central burners are required for carbon combustions.

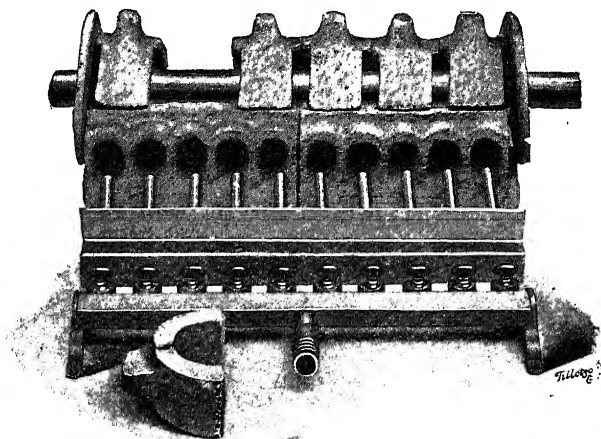


Fig. 9.—Combustion furnace.

(2) A Berzelius gasholder of 3 or 4 litres capacity (Fig. 10). Any other suitable gasholder may be used.

(3) A Dufty tower (Fig. 11) for purifying and drying the air.* The bottom portion is charged with about 200 c.c. of a strong solution of potas-

* See contribution by Lawrence Dufty, *Chemical News*, 19th June, 1903.

sium hydrate (caustic potash), and the upper part is loosely packed with sticks of potassium hydrate supported on the perforated plate. On bubbling air through the solution, carbon dioxide and other



Fig. 10. —Gasholder.

impurities are absorbed, and, on passing through the chamber containing the solid potassium hydrate, the air is dried.

(4) A glass tower (Fig. 12) containing granular soda lime and fused granular calcium chloride. This is used to make sure that the air is thoroughly purified and dried. The fused salts are supported on a piece of copper gauze placed at the constriction above the inlet. The stopper may be turned so as to shut off air or prevent its passage.

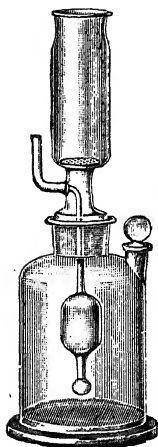


Fig. 11.—Dufty tower.

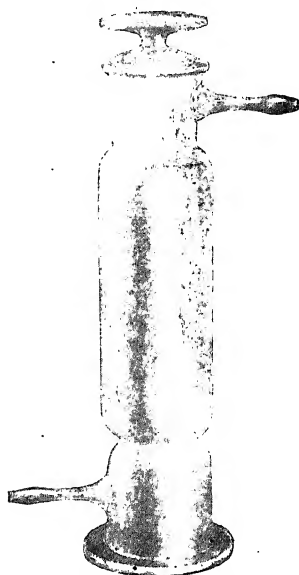


Fig. 12.—Glass tower.

A U-tube with stopper-taps (Fig. 13) may be used instead of the tower.

(5) A porcelain combustion tube 26 inches long by $1\frac{1}{8}$ inch diameter, with an enlargement at each end for tight-fitting one-holed india-rubber

bungs. Only a small part of the tube requires to be heated, but a long tube is selected, so that the bungs will not be decomposed by the heat.

(6) An Arnold's absorption bulb, with the addition suggested by Dufty (Fig. 14). This is charged with about 15 c.c. of a nearly saturated solution of chromic acid in pure dilute sulphuric acid—water 9 : acid 11—and is intended to retain sulphur compounds.

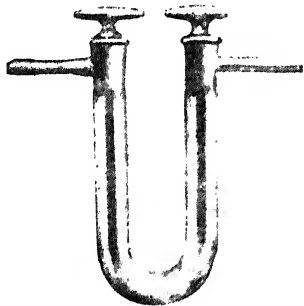


Fig. 13.--U-tube, with combined stoppers and taps

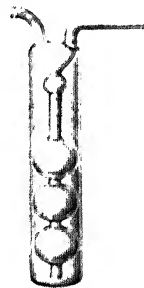


Fig. 14.-- Arnold absorption bulb.

(7) A drying tower, same as No. 4 (Fig. 12), containing fused granular calcium chloride.

(8) A Mohr's or Geissler's absorption bulb (Fig. 15), each of the three lower bulbs of which is half-filled with a solution of potassium hydrate. This solution is made by dissolving 25 grammes of pure potassium hydrate in water, and making up with more water to 60 c.c.

The ground-on tube at the outlet end is charged with fused granular calcium chloride.

Potash solution is drawn into the bulbs by dipping the free end (B) into solution contained in a beaker and sucking from a rubber tube (with a glass mouthpiece) attached to the outlet (A). The inside of the inlet tube is then dried by means of a spill of filter-paper, and the remainder of the apparatus is wiped dry by a cloth which does not leave fluff on the glass.

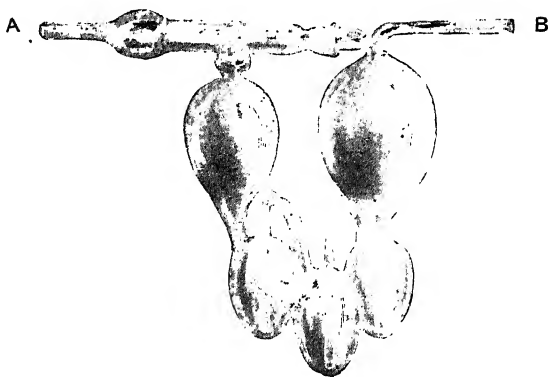


Fig. 15.—Bulb for absorption of carbon dioxide, with drying tube.

(9) A drying tower, same as No. 4 (Fig. 12), containing fused granular calcium chloride.

The several pieces (Nos. 2 to 9) are to be connected to each other by means of glass tubing (with ends fused round in a flame) and rubber tubing. The ends of the pieces of glass apparatus or the ends of the glass connections should be brought close to each other.

(10) Fireclay or magnesite combustion boats,

as made by the Morgan Crucible Co., Battersea Works, London. A stock of these boats should be highly heated in a good muffle furnace for two or three hours, and, when cooled a little, placed in a desiccator, and kept there till required.

(11) A roll of oxidised copper gauze. This is made by forming a loop at each end of a piece of stout copper wire and winding a length of copper gauze—say, 7·5 or 10 cm. (about 3 or 4 inches) broad—round the wire till a roll is formed of about 2·5 cm. (or about 1 inch) diameter. The roll is firmly bound with fine copper wire, and oxidised by heating in a current of air. It is placed in the combustion tube to make sure of all the carbon being oxidised to dioxide. In one steel work, granular roasted manganese ore is loosely packed in the combustion tube between two plugs of ignited asbestos, and is found to be effective in completing the oxidation of the carbon.

(12) A stout iron wire, about 2 feet long, bent at one end, and having a loop to indicate the distance to which the boats are to be pushed into the porcelain tube.

(13) Glass tubing for making connections.

(14) A number of good india-rubber junction or connecting pieces.

(15) A number of stoppers, made of small pieces of glass rod and india-rubber tubing. All ends of glass tubing and glass rod should be rounded in a flame.

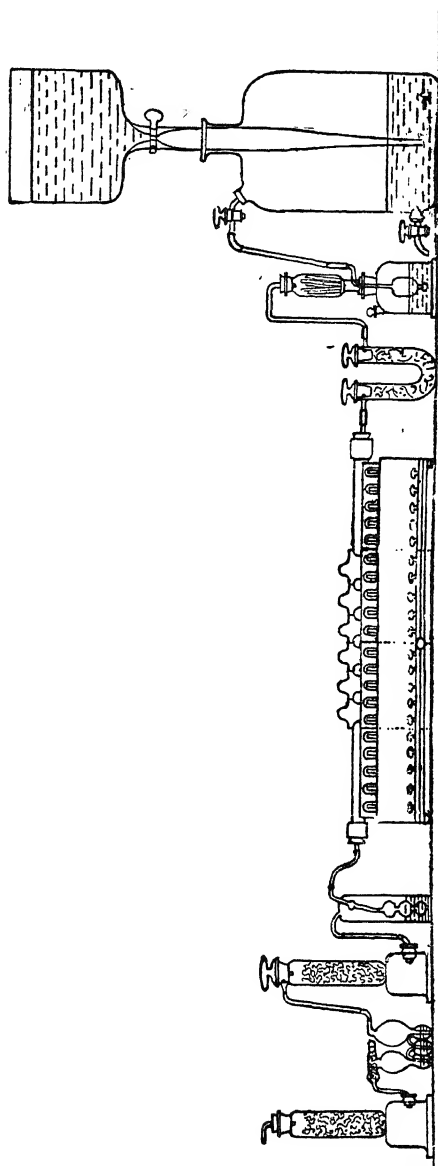


Fig. 16.—Arrangement of apparatus for carbon combustion.

Details of the Process.—Collect the apparatus and charge the towers and bulbs as directed.

With good india-rubber connections, join the various pieces of apparatus in the order stated, and test the tightness of the whole by closing the tap of the gasholder and attaching the No. 9 tower (Fig. 12) to a rubber tube connected to an aspirator.

Turn the stoppers of all the towers so as to leave a free passage for air.

Cause the aspirator to work gently. If all the connections are sound, air will soon cease to be drawn through the absorption bulbs. Make good any defective connections. When satisfied that the apparatus is in good working order, cautiously detach the tube to the aspirator, open the tap of the gasholder, and pass a gentle current of air through the whole system for about three minutes.

Close the tap of the gasholder.

Detach the No. 8 absorption bulb (Fig. 15), close the ends with stoppers, place in the balance case, and allow to remain for about fifteen minutes.

Push the roll of oxidised copper gauze into the combustion tube to a position beyond the middle of the tube.

Proceed to heat the combustion tube by lighting alternate burners, while the taps are turned half on, under the roll of oxidised copper gauze and the middle part of the porcelain tube, where the charged boat is to be kept during the combustion. After a few minutes light the burners between those already lit, and, after a time, turn all these burners full on,

and place the arched covering tiles over the hot part of the porcelain tube.

Weigh off 2.727 grammes of the sample of steel, which should be in the form of drillings or turnings in short pieces not more than 0.25 mm. thick.

Mix the weighed portion with well-burned powdered magnesite brick, and spread it in a combustion boat containing a thin layer of thoroughly calcined manganese ore.

Take the stoppers off the absorption bulb (Fig. 15), weigh, and note the weight.

Connect the weighed bulb with towers 7 and 9.

Place the charged boat in position in the hot combustion tube.

Press the india-rubber bung firmly into position.

Allow a current of air to issue from the gasholder, and pass through all the apparatus.

Maintain the furnace at a good red heat, and allow combustion to proceed for two hours.

Detach the No. 8 absorption bulb (Fig. 15) first from the No. 7 tower and then from the No. 9 tower, stopper the bulb, and place it in the balance case.

After about fifteen minutes take off the stoppers, again weigh the bulb with the absorbing solution, and note the weight.

Calculate the percentage of carbon.

EXAMPLE—

Weight of bulb, &c., after combustion,	43.7351	grms.
" " before "	43.7169	"
Weight of carbon dioxide absorbed,	0.0182	"

Percentage of C in $\text{CO}_2 = 27.27$.

$$\frac{27.27}{2.727} \times 0.0182 = 0.18.$$

0.18 = percentage of carbon in the sample.

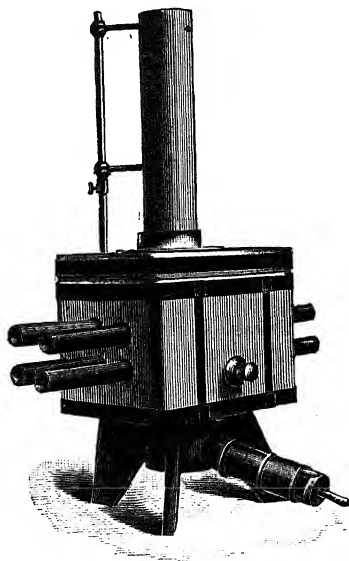


Fig. 17.—Huxley furnace.

If oxygen is used instead of air, the combustion may be completed in thirty minutes after action has begun. For a time no gas passes through the bulbs, as all the oxygen passed in combines to form carbon dioxide, which is all absorbed in the potash solution. When all the carbon has been oxidised, the oxygen bubbles through the Dufty tower and the weighed absorption bulb at the same rate.

To obtain reliable results by combustion practice is necessary. Even an analyst who has had experience in this class of work should make an estimation on a steel of known percentage of carbon before making an assay of an unknown sample—if he has been out of practice.

It is usual, where many estimations by combustion are regularly made, to keep four assays going simultaneously. For this purpose a Huxley tube furnace set on a Griffin's radial burner (Fig. 17) is used. The porcelain combustion tubes pass through the openings provided for that purpose. A cylindrical fireclay muffle surrounds the combustion tubes, so as to ensure uniformity of heating and obviate any fracture of the tubes. A central hole, used for lighting the burner is closed by a clay plug when the furnace is in use.

Electrically heated furnaces are now frequently used, and are very convenient. The evolved carbon dioxide may be absorbed in a tube loosely packed with two parts soda-lime and one part caustic soda mixed with a little dry phenolphthalein to act as an indicator of approaching saturation or ineffectiveness.

NOTES ON CARBON COMBUSTIONS.

For the estimation of carbon by combustion, the methods in use are :—

- (1) Direct combustion, as described in the preceding pages.
- (2) Direct combustion, as in (1), preceded by separation of the carbon.
- (3) Moist oxidation, preceded by separation of the carbon, as in (2).

The direct combustion method, as detailed in the foregoing pages, is applicable to wrought iron, to all kinds of steel, to ferro-chrome, spiegel-eisen, ferro-manganese, &c., but cannot be depended on to yield good results when estimating the carbon in grey pig iron, silico-ferro, &c.

“When being burnt, theoretically every particle should be isolated from its fellow so that the oxygen in passing over the material may act on every side of them. In practice this is impossible, but a near approach to it can be effected by mixing the drillings with granulated particles of crushed magnesite brick or with granulated calcined manganese ore. When the drillings consist entirely of spiral pieces there is no need for any admixture whatever, as the oxygen can then act upon all parts without the intervention of any mechanical support. If, however, the particles of steel or metal are in fine powder, it is imperative that this mechanical suspension should be effected.”—*Stead.*

In the hands of a competent analyst possessing

practical acquaintance with combustions, accurate and rapid results may be regularly obtained.

For the correct estimation of carbon in grey pig iron, ferro-silicon, &c., it is necessary that, prior to combustion, a residue containing all the carbon should be obtained. For this purpose the weighed sample is dissolved in an acidified solution of copper-potassium chloride, and the carbonaceous residue is collected on a filter of prepared asbestos fibres.

There is always an evolution of hydrocarbon gases during solution of steels, &c. This, of course, leads to the results being invariably low. The higher the percentage of carbon in a steel, the greater is the loss due to escaping hydrocarbons.

The same steel has been proved to yield a larger amount of hydrocarbon gases after hardening than was evolved in an unhardened state.* Hardened steels must therefore be annealed before being dissolved in acidified copper-potassium chloride.

* Dillner, *Iron and Steel Institute Journal*, vol. ii., 1904, p. 255.

SEPARATION OF CARBON FOR ESTIMATION BY COMBUSTION.

Outline of the Process.—On dissolving a sample containing both combined and graphitic carbon with acid, the combined carbon is converted into hydrocarbons which escape in the gaseous state. This escape may be prevented by treating the sample with copper chloride solution. The copper precipitated while dissolving is more easily soluble in an acid solution of copper-potassium chloride.

The carbonaceous residue is collected and washed on a filter which is made by carefully packing a plug of prepared asbestos on the perforated disc of a Reinhardt funnel (Fig. 18). The finely-shredded asbestos is washed to get rid of chlorides, dried, and ignited before being packed in the funnel. A filter pump is used in connection with this.

Details of the Process.—Weigh off a portion of the sample, which should be in the form of shavings or in powder. These should neither be too fine nor too coarse. For ordinary pig iron 1.3635 gramme may be weighed off; a greater or lesser quantity should be taken for materials containing less or more carbon.

To 1.3635 gramme in an 11 × 11 cm. (about $4\frac{1}{2} \times 4\frac{1}{2}$ inches) beaker, add 200 c.c. of an acidified solution of copper-potassium chloride (see p. 410).

Heat gently to promote circulation, stir frequently, and finally boil until solution of the iron is complete

and no trace of free copper remains. Blair hastens solution by stirring the liquid by a machine.

When the precipitated copper is all, or very nearly all, dissolved, run a little of the acidulated double chloride around the inside of the beaker, directing by means of the stirring rod, wash the rod over the beaker with a jet of water, and let the beaker stand for a few minutes to allow the carbonaceous matter to settle.



Fig. 18.—Reinhardt funnel for asbestos plug.

Collect this residue on the asbestos plug. Do not allow the lip of the beaker to touch the surface of the liquid in the plug, or a film of carbonaceous matter will run up the inside of the beaker.

Wash several times with water containing a little hydrochloric acid and some fine, ignited asbestos fibres. The addition of the fibres, suggested by Barba, promotes the settling of the carbonaceous matter and prevents the clogging of the filter.

The carbonaceous residue from puddled iron, spiegel-eisen, ferro-manganese, and ingot steel usually washes like sand ; but that from steel which has been hardened, tempered, hammered, or rolled is apt to be more or less gummy, stopping the filter and rendering the filtration long and tedious. It is also apt to adhere more or less to the sides of the beaker, and must be wiped off by a small wad of ignited, fibrous asbestos held in a pair of fine platinum-pointed forceps. This wad is then placed on the asbestos filter or plug.

Wash three or four times more, using pure distilled water.

Allow to drain well and then stop the action of the filter pump. Place a layer of prepared asbestos over the washed residue, so as to form a sandwich with the carbon, &c., in the centre.

Push the whole out of the funnel

If intended for dry combustion, place in a hot-air bath, and, when dry, pack in a fireclay or magnesite boat, and proceed with the combustion as directed on pp. 105, 106.

If the carbon is to be oxidised by the wet process, continue the determination as directed on the next page.

ESTIMATION OF CARBON BY WET OXIDATION.

Apparatus Required.

(1) A gasholder as shown by Fig. 10, p. 188. This is used for testing the apparatus.

(2) A Dufty tower, as shown by Fig. 11, p. 189. This is charged as directed on pp. 187 and 188.

(3) A glass tower, as shown by Fig. 12, p. 189, containing granular soda lime and fused granular calcium chloride.

(4) A 250 c.c. conical flask with a tight-fitting two-hole rubber cork, carrying a funnel with stop-cock, and a delivery tube.

(5) An Argand burner, on which the conical flask is set.

To the delivery tube, the following, as used by Stead,* should be attached by rubber connecting pieces in the order named, viz. :—

A series of U tubes containing respectively anhydrous copper sulphate, cuprous chloride, chromic acid, and calcium chloride. To the last-named, the charged and weighed Geissler potash bulbs (Fig. 15, p. 191) are attached, and a U tube or tower containing granular calcined calcium chloride is connected to the outlet end of the bulb.

Connect the various parts in series.

Tare the charged Geissler bulbs and note the weight.

* *Iron and Steel Institute Journal*, vol. ii., 1904, p. 260.

Connect the bulbs, and test the efficiency of the system by drawing a current of dried and purified air through the whole series. Close the stopcock of the funnel and continue the aspiration. When satisfied that all the connections are tight, open the stopcock and draw dried and purified air through the whole system for a few minutes. Detach the Geissler bulb, wipe with a clean piece of silk, stopper the ends with glass rod and rubber pieces, and place the whole in the balance case. After about ten minutes, re-weigh. The weights should not show either increase or decrease.

When satisfied that all the apparatus is in good order, tare the Geissler bulb again (if necessary) and go on with the oxidation.

Transfer the still moist sandwich containing the carbonaceous residue to the 250 c.c. conical flask.

Add 15 c.c. of 50 per cent. chromic acid solution (see p. 339).

Press the cork carrying the stoppered funnel and delivery tube into the neck of the flask, and quickly make the necessary connections.

Measure 40 c.c. of 1.8 specific gravity sulphuric acid into the stoppered funnel.

Allow the acid to flow into the flask in small instalments, closing the tap between each.

Heat, gently at first, and later more strongly, until white fumes appear in the flask.

Detach the Geissler bulb, close the ends, wipe the bulb, place in the balance case, and allow to remain about fifteen minutes.

Take off the stoppers, and again weigh the bulb.

Calculate the percentage.

$$\frac{\left\{ \begin{array}{l} \text{Weight of carbon dioxide} \\ \text{absorbed} \times 27.27 \end{array} \right\}}{\text{Weight of sample taken}} = \left\{ \begin{array}{l} \text{percentage of carbon} \\ \text{in the sample.} \end{array} \right.$$

Knut A. Gunnar Dillner (Stockholm) introduces a platinum tube—which is kept red-hot during the oxidation—between the conical flask and the tube containing calcium chloride, which is placed before the Geissler bulb. The U tubes containing copper sulphate, cuprous chloride, and chromic acid are not required. The evolved gases are passed through the red-hot platinum tube, and very satisfactory results are obtained.

ESTIMATION OF CARBON IN PIG IRON, FERRO-SILICON, &c.

Graphitic carbon may be estimated by collecting the insoluble residue obtained as directed on pp. 13 and 14 on an asbestos filter (see p. 153). After washing, the residue—which consists of graphite and silica, with perhaps a little iron—is dried and placed in a Battersea fireclay or magnesite combustion boat, which is then pushed into a hot combustion tube. A high temperature is maintained to ensure the complete combustion of the graphite.

The apparatus is arranged as previously described, and all the customary precautions are taken.

The percentage is calculated from the weight of the carbon dioxide absorbed in the Geissler bulb.

ESTIMATION OF CARBON IN ALLOY STEELS.

In estimating, by direct combustion, the carbon in steels containing chromium, titanium, or tungsten, the contents of the combustion boat should be heated to 1,500° C. for thirty minutes after the metal has ceased to "burn." By this prolonged heating, slightly higher results are obtained than by the usual methods.

ESTIMATION OF CHROMIUM.

CHROMIUM IN STEEL.—STEAD'S METHOD.

Outline of the Process.—The sample, preferably in moderately-fine drillings or turnings, is dissolved in sulphuric acid and oxidised by permanganate. Hydrochloric acid is added, and the solution is boiled till all chlorine is driven off. To the clear solution, excess of ferrous salt in known quantity is added. The oxidation of ferrous iron due to the chromium in the steel, is ascertained, by difference, on titrating with standard dichrome solution (see pp. 131 to 137 for details of dichrome titrations).

Details of the Process.—Weigh off 2 grammes of the steel drillings or turnings. For steels containing a small percentage of chromium, a larger quantity of sample should be taken.

Transfer the weighed portion to a beaker of about 1,000 c.c. capacity.

Add 30 c.c. of dilute sulphuric acid [1 of acid (sp. gr. 1.84) to 3 of water].

Pour on to the sample in the beaker.

Cover with a clock glass.

Set the beaker on a hot plate and allow to remain until crystals begin to form in the solution.

Wash down any crystals which may have crept up the sides of the beaker.

Add about 70 c.c. of hot water.

Filter, collecting the filtrate in a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Dilute with about 200 c.c. of water.

Add a solution of 0.5 gramme of potassium permanganate in a little water.

Boil for ten minutes. At this stage the liquid should still be of a pink colour. If not, add potassium permanganate crystals until it is so.

Mix 40 c.c. of hydrochloric acid (1.16 sp. gr.) with an equal bulk of water, and add to the liquid in the beaker. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil, and gently continue the boiling till the brown peroxide dissolves.

Add 150 c.c. of boiling water, and boil till about 100 c.c. of water has evaporated.

The solution should then be free from chlorine. This may be confirmed by holding a piece of litmus paper in the vapour from the basin. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration:—

Standard dichrome solution (see pp. 131 to 134).

A burette graduated in one-tenths.

A burette stand.

A glass stirring rod about 20 cm. (or 8 inches) long.

A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of "drop reaction" filter-paper.

A glass or porcelain dish with a freshly-prepared solution of potassium ferricyanide. About 0.1 gramme may be dissolved in 100 c.c. of water.

A glass stirring rod, about 10 cm. (or about 4 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution, and run off the solution into a sink.

Again fill the burette with standard dichrome solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Weigh off about 4 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the

ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example:—

Sample of steel taken . . . = 2.000 grammes.

" Mohr's salt taken . . . = 4.007 ..

Iron in Mohr's salt $\frac{4.007 \times 14.26}{100} = 0.5714$ gramme.

Dichrome solution required = 23.10 c.c., of which each c.c. = 0.01013 gramme of iron.

$$23.1 \times 0.01013 = 0.234.$$

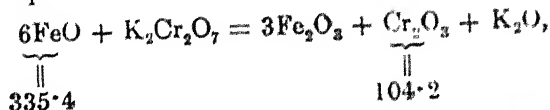
Grammes.

Iron in Mohr's salt = 0.5714

" represented by the standard dichrome
used = 0.2340

" oxidised per chromium in the example = 0.3374

Equation—



which shows that in this reaction 335.4 parts, by

weight, of iron are equivalent to 104.2 parts, by weight, of chromium. Then

$$\frac{104.2 \times 100}{335.4} = 31.067.$$

$$31.067 = \text{Factor.}$$

$$\text{Log } 31.067 = 1.4922993.$$

The percentage of chromium is found by multiplying the "iron oxidised" by this factor and dividing by the amount of sample taken

In this instance,

$$\frac{0.3374}{2} \times 31.067 = 5.24.$$

5.24 = percentage of chromium in the sample of steel.

ESTIMATION OF CHROMIUM IN FERRO-CHROME.—
SANITER'S METHOD.

Outline of the Process.—The sample for analysis should be finely pounded and mixed well. A portion should then be taken and pulverised in an agate mortar, so that the whole of it will pass through a sieve of 10,000 holes per square inch = 100 wires each way per square inch. The weighed sample is fused at a moderate temperature in a mixture of sodium and barium peroxides. A soluble "melt," containing the chromium, iron, &c., of the sample in their highest state of oxidation, is thus obtained.

This is dissolved, and when all the materials for a dichrome titration are ready, a weighed quantity of a substance containing a known amount of ferrous iron—which must be in excess—is also dissolved, and the solution is titrated with standard dichrome solution. The oxidation of the ferrous iron, due to the chromium in the ferro-chrome, is thus ascertained by difference.

Details of the Process.—Weigh off about 4 grammes of sodium peroxide, and about 0·75 gramme of barium peroxide.

Mix the weighed portions, and transfer to a nickel capsule of 7·5 cm. (about 3 inches) diameter.

Weigh off accurately about 0·3 to 0·5 gramme of the pulverised sample, and note the weight taken.

Add to the peroxides in the nickel capsule, and mix all well.

Hold the capsule by means of crucible tongs, or on a pipe-clay support fastened to a convenient handle, in the flame of a good Bunsen burner until the mass begins to melt. The temperature should be just short of visible red. Then impart a circular motion to the capsule while keeping it in the flame and taking care not to allow the solids to settle to the bottom. Fusion may be effected in a muffle at a dull red heat.

Continue the fusing for about three minutes. This should yield a very liquid melt.

Allow the capsule and contents to cool.

Place in a glazed porcelain basin of 18 cm. (about 7 inches) diameter.

Pour water into the nickel capsule, and allow the melt to dissolve.

Pour the solution into the porcelain basin.

Rinse the remainder from the nickel capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the nickel capsule any still-clinging melt may be loosened.

Add about 300 c.c. of hot water to the contents of the porcelain basin.

Add about 0.3 gramme of potassium permanganate crystals. The quantity added should produce a strong pink colour, which does not disappear until gently boiled for more than ten minutes after the addition of the dilute hydrochloric acid noted below.

Mix 40 c.c. of hydrochloric acid (1.16 sp. gr.) with an equal bulk of water, and add to the liquid in the basin. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil till clear.

Add 150 c.c. of hot water.

Boil for ten minutes to make sure that all chlorine has been driven off. This may be confirmed by holding a piece of litmus paper in the vapour from the basin. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration:—

Standard dichrome solution (see pp. 131 to 134).

A burette graduated in one-tenths.

A burette stand.

A glass stirring rod about 20 cm. (or 8 inches) long.

A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of "drop reaction" filter-paper.

A glass or a porcelain dish with a freshly-prepared solution of potassium ferricyanide. About 0.1 gramme may be dissolved in 100 c.c. of water.

A glass stirring rod, about 10 cm. (or about 4 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution, and run off the solution into a sink.

Again fill the burette with standard dichrome solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Place on the slab at intervals a series of drops of the ferricyanide solution.

Weigh off about 5.5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mingling of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example:—

EXAMPLE OF CALCULATION.—

Sample of ore taken . . . = 0·435 gramme.
 „ Mohr's salt taken . . = 4·7405 grammes.
 Iron in Mohr's salt taken

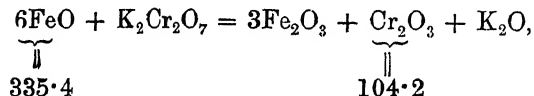
$$= \frac{4\cdot7405 \times 14\cdot26}{100} = 0\cdot676 \text{ gramme.}$$

Dichrome solution required = 11·18 c.c., of which
 each c.c. = 0·0102 gramme of iron.

$$11\cdot18 \times 0\cdot0102 = 0\cdot1140.$$

Iron in Mohr's salt . . . = 0·676 gramme.
 „ represented by the standard
 dichrome used, . . . = 0·114 „
 „ oxidised by chromium in the
 sample . . . = 0·562 „

Equation—



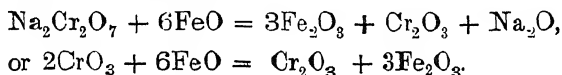
which shows that in this reaction 335·4 parts, by weight, of iron are equivalent to 104·2 parts, by weight, of chromium. Then

$$\frac{0\cdot562 \times 104\cdot2 \times 100}{335\cdot4 \times 0\cdot435} = \frac{0\cdot562}{0\cdot435} \times 31\cdot067 = 40\cdot139.$$

40·14 ÷ percentage of chromium in the sample
 of ferro-chrome.

ESTIMATION OF CHROMIC OXIDE IN CHROME IRON ORE.
SANITER'S METHOD.

Outline of the Process.—The finely-ground, weighed sample is heated along with sodium peroxide in a nickel capsule. The "melt" is dissolved, acidified with hydrochloric acid, and peroxidised by permanganate. Chlorine is driven off by boiling. All the oxidisable components of the ore are then in their highest state of oxidation. A known quantity—which must be in excess—of ferrous salt is dissolved in the solution and is acted on by the chromate from the ore, which converts an equivalent amount of ferrous oxide to the ferric state, thus:—



The amount of ferrous oxide unacted on is determined by titrating with standard dichrome solution as in the estimation of iron (but without further addition of ferrous salt), as directed on pp. 134 and 135 for details of bichrome titrations.

Details of the Process.—The first stage is the fusing of the finely-ground sample so as to obtain a good melt. For this purpose two good methods are available.

(A) Weigh off about 3 grammes of sodium peroxide.

Transfer the weighed portion to a nickel capsule of about 7.5 cm. (3 inches) diameter.

Weigh off accurately about 0.5 gramme of the finely-ground sample—the sample should be ground

as fine as possible in an agate mortar—and note the amount taken.

Add the weighed portion to the sodium peroxide in the capsule, and mix thoroughly.

Hold the capsule, by means of crucible tongs or on a pipeclay support fastened to a convenient handle, in the flame of a good Bunsen burner until the mass begins to melt. The temperature should be just short of visible red. Then impart a circular motion to the basin while keeping it in the flame, and taking care not to allow the ore to settle to the bottom. Fusion may be effected in a muffle furnace at a dull red heat.

Continue the fusing for about three minutes. This should give a very liquid melt.

Alternatively the following method of fusing may be followed:—

(B) Messrs. James H. Walton, Junr., and Herman A. Scholz give, in the *American Chemical Journal*, xxxix., No. 7,* details of a method for the rapid decomposition of chrome iron ore. The mixture prescribed by them is—

0.5 gramme chrome iron ore (through 200 mesh seive).

8.0 grammes sodium peroxide.

0.3 gramme potassium persulphate.

2.0 grammes iron pyrites.

0.3 gramme magnesium powder.

The correct proportions appear to depend on the

* See *Chemical News*, 14th August, 1908.

richness of the pyrites. With rich pyrites the reaction is violent. But it is not difficult to adjust the proportions.

The mixture is placed in a nickel capsule and ignited by means of a thin piece of magnesium wire. Very little damage is done to the capsule, and a nice liquid melt is easily obtained.

Whichever method may have been adopted—either A or B:

Allow the capsule and contents to cool.

Place in a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Pour water into the nickel capsule and allow the melt to dissolve.

Pour the solution into the porcelain basin.

Rinse the remainder from the nickel capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the capsule, any still-clinging melt may be loosened.

Add about 230 c.c. of hot water to the contents of the porcelain basin.

Add also 50 c.c. of water in which a few crystals of potassium permanganate have been dissolved.

The theoretical amount of permanganate required to oxidise 1 gramme of FeO to Fe_2O_3 is 0.44 gramme.

Enough permanganate should be added to impart to the liquid a decided pink colour which does not disappear until gently boiled for more than ten minutes after the addition of the dilute hydrochloric acid noted below.

Mix 40 c.c. of hydrochloric acid (1.16 sp. gr.) with an equal bulk of water, and add to the liquid in the

basin. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil till clear.

Add 150 c.c. of hot water.

Boil for ten minutes, to make sure that all chlorine has been driven off. This may be confirmed by holding a piece of litmus paper in the vapour from the beaker. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration :—

Standard dichrome solution (see pp. 131 to 134).

A burette graduated in one-tenths.

A burette stand.

A glass stirring rod about 20 cm. (or 8 inches) long.

A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of "drop reaction" filter-paper.

A glass or porcelain dish with a freshly-prepared solution of potassium ferricyanide. About 0.1 gramme may be dissolved in 100 c.c. of water.

A glass stirring rod, about 10 cm. (or about 4 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution, and run off the solution into a sink.

Again fill the burette with standard dichrome solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Place on the slab at intervals a series of drops of the ferricyanide solution.

Weigh off about 4.5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mingling of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example:—

EXAMPLE OF CALCULATION.—

Weight of ore taken . . . = 0.5031 gramme.

„ Mohr's salt taken = 5.1166 grammes.

Iron in Mohr's salt taken

$$= \frac{5.1166 \times 14.26}{100} = 0.72963$$

Dichrome solution required = 22.6 c.c., of which
each c.c. = 0.0102 gramme of iron.

$$22.6 \times 0.0102 = 0.23052.$$

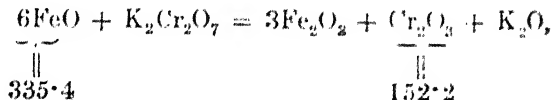
Iron in Mohr's salt . . . = 0.72963 gramme.

„ represented by the standard

dichrome used, . . . = 0.23052 „

„ oxidised by Cr_2O_3 in the . . .
sample of ore . . . = 0.49911 „

Equation—



which shows that, in this reaction, 335.4 parts. by weight, of iron are equivalent to 152.2 parts, by weight, of chromic oxide. Then—

$$\frac{0.4991 \times 152.2 \times 100}{335.4 \times 0.5031} = \frac{0.4991}{0.5031} \times 45.38 = 45.02.$$

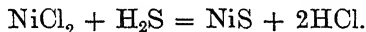
45.02 = percentage of Cr_2O_3 in the sample of ore

ESTIMATION OF NICKEL.

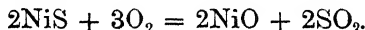
NICKEL IN STEEL—GRAVIMETRIC METHOD.

SEPARATING AS SULPHIDE, AND WEIGHING THE
ROASTED RESIDUE.

Outline of the Process.—The weighed sample of the steel is dissolved, and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a bulky precipitate consisting of basic hydrate and acetate of iron is formed, and the solution containing the nickel is separated on filtering and washing. The solution is concentrated by evaporation. This second precipitate is dissolved in acid, the solution is neutralised, and the iron is reprecipitated, drained into a filter, and washed. The second filtrate and washings are also concentrated, and, if necessary, the two concentrates are filtered, all the liquid being collected in a large flask, and ammonia added. Sulphuretted hydrogen is then passed into the liquid. This causes the formation of nickel sulphide—



The precipitate is collected on a filter, washed dried, and roasted till all the nickel sulphide is converted into oxide—



The percentage of nickel is calculated from the weight of the nickel oxide.

Details of the Process.—Weigh off 2.5 grammes of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 35 c.c. of 1.42 specific gravity nitric acid along with 15 c.c. of water.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 15 c.c. of hot water.

Boil.

Add ammonia liquor till a slight permanent precipitate forms and remains in the hot liquid even after vigorous shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 400 c.c. of cold water.

Add 45 c.c. of ammonium acetate solution (see p. 162).

Boil briskly over the flame of a 16 mm. (about $\frac{5}{8}$ -inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is risky.

Prepare a 28 cm. (about 10-inch) folded filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large filter stand (see Fig. 7, p. 36). Set under it a Berlin basin 7 inches diameter, or larger.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove the flask till the brisk action ceases; replace on the tripod, and allow the rapid boiling to continue. It may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear colourless liquid should drain away quickly when on the filter.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask twice with hot water and pour the rinsings on to the filter. Allow the liquid to drain off thoroughly into the basin.

Wash twice with hot water, collecting the washings in the basin.

Set the basin containing the filtrate and washings over a Bunsen burner, or on a hot plate, so as to evaporate the liquid to small bulk.

Place the flask in which solution of the weighed sample had been effected under the stem of the funnel.

Dissolve the iron precipitate on the filter by means of hot hydrochloric acid and water, collecting all the solution and washings in the flask.

Neutralise with ammonia liquor as before.

Add 45 c.c. of ammonium acetate solution (see p. 162).

Boil, filter, and wash as before, collecting the filtrate and washings in a Berlin basin of 18 cm. (about 7 inches) diameter.

Evaporate the solution to small bulk, and add it to the solution which has been evaporating in the other basin.

If necessary, filter and wash.

Collect the concentrated solutions in a large conical flask, add about 10 c.c. of ordinary pure acetic acid, and pass a rapid stream of sulphuretted hydrogen through the liquid until a precipitate ceases to form and the solution smells strongly of the gas.

Boil off the excess of sulphuretted hydrogen.

Filter through a 12.5 cm. Swedish filter and wash thoroughly with hot water.

The washed residue may be dissolved in hydrochloric acid and again treated with sulphuretted hydrogen to cause the reprecipitation of nickel sulphide, which should be collected on a filter and washed as before. Or the nickel in the solution may be precipitated by sodium hydrate, the precipitate collected, washed, dried, ignited, and weighed as nickel oxide.

The filtrate and washings may be used for the estimation of manganese.

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace which is at a red heat. Allow to remain in the hot muffle till the roasting is completed—45 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Repeat the roasting for about 30 minutes.
 Allow to cool in a desiccator and reweigh.
 Calculate the result.

Pure nickel oxide contains 78.581 per cent. of nickel, and when 2.5 grammes are taken for the estimation the factor for finding the percentage is—

$$\frac{78.581}{2.5} = 31.432.$$

$$\text{Log } 31.432 = 1.4973720.$$

EXAMPLE OF CALCULATION—

Weight of precipitate + crucible

	+ ash . . .	= 18.9031 grammes.
„	crucible . . .	= 18.8264 „
		<hr/>
„	precipitate + ash . . .	= 0.0767 gramme.
„	ash . . .	= 0.0008 „
		<hr/>
„	precipitate . . .	= 0.0759 „
		<hr/>

$$0.0759 \times 31.432 = 2.386.$$

$2.39 \div$ percentage of nickel in the sample of steel.

ESTIMATION OF NICKEL IN STEEL.

GRAVIMETRIC DIMETHYLGLYOXIME METHOD.

Outline of the Process.—This excellent method by O. Brunck (see *Zeit. f. angewandte Chemie*, 1907, vol. ii.) is based on the fact that when an alcoholic solution of dimethylglyoxime is added to a neutral or slightly alkaline solution containing nickel, a voluminous scarlet-red precipitate containing all the nickel is formed. This is collected on a filter, and is easily washed. The precipitate is then washed into a tared basin, dried on a water bath, and weighed. From the weight of the pure dried precipitate the percentage of nickel present is calculated.

Details of the Process.—Weigh off 1 gramme of the drillings from the sample.

Transfer to an 800 c.c. Bohemian or Jena beaker.

Dissolve in the smallest workable quantity of 1.16 specific gravity hydrochloric acid—20 c.c. is usually sufficient—and boil, with further small additions of hydrochloric acid, to make sure of the iron being in the ferric state.

Filter if necessary, collecting the filtrate (and washings) in a 500 c.c. beaker. Dilute to about 350 c.c.

Wash well with warm water.

Add about 1 gramme of pure tartaric acid either in crystals or in solution.

Heat the solution to about 50° C.

Add enough dimethylglyoxime solution (see p. 340) to precipitate all the nickel present. Good

results were obtained on working with the following quantities:—

Steel containing about 0·5 per cent. of nickel,	15 c.c.
" 1·0 " "	20 "
" 1·5 " "	30 "
" 2·0 " "	40 "
" 2·5 " "	45 "
" 3·0 " "	50 "
" 3·5 " "	55 "

Add ammonia liquor until the solution is faintly alkaline—excess must be avoided—and stir the solution well. This will cause a precipitation of a scarlet-red precipitate, which is a little difficult to see at first in the deep coloured solution. Dimethylglyoxime precipitates nickel only; mixed impurities are easily separated by washing.

Collect precipitate on a 15 cm. smooth filter-paper.

Wash the precipitate thoroughly with warm water.

Open out the filter-paper, and, with a fine-spout wash bottle containing warm water, wash the precipitate into a 7·5 cm. (about 3 inches) diameter tared porcelain basin.

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the outside of the basin with a clean cloth which does not leave fluff.

Allow the basin and precipitate to cool in a desiccator.

Weigh, and calculate the result.

The precipitate, when thoroughly washed and

dried on a water bath, consists of $C_8H_{14}N_4O_4Ni$, and contains 20.332 per cent. of nickel.

$$\text{Log } 20.332 = 1.3081801.$$

EXAMPLE—

Weight of basin + precipitate = 23.4463 grammes.

„ basin . . . = 23.3180 „

„ precipitate . . . = 0.1283 gramme.

$$0.1283 \times 20.332 = 2.61.$$

2.61 = percentage of nickel in the sample of steel.

ESTIMATION OF NICKEL IN STEEL BY ELECTRIC CURRENT.

Weigh off about 0.3 gramme of the steel—which should be in the form of fine turnings or drillings—and note the weight taken.

Transfer the weighed sample to a beaker 11.5×7.5 cm. ($4\frac{1}{2}$ inches deep \times 3 inches) diameter.

Dissolve in minimum excess of nitric acid.

Cautiously add strong sulphuric acid, and evaporate till plentiful fumes appear and crystals form in abundance in the solution.

Cautiously add about 100 c.c. of hot water.

Add ammonia liquor till all the iron is precipitated, then add a slight excess.

Digest for 15 minutes or more on a hot plate.

Connect the positive pole of a battery or accumu-

lator to a platinum spiral, and the negative pole to a weighed platinum gauze cone. Rotating cones, &c., are preferred to stationary ones.

Immerse the couple in the beaker containing the solution.

Allow the electric current to pass through for three hours or more, beginning with 1 ampere and increasing, at intervals of half-an-hour, up to 2 amperes, allowing full strength for the last half hour or more.

Maintain about 4 volts all the time.

Withdraw the beaker containing the solution.

Wash, with water, the cone, &c.

Disconnect.

Wash the cone, firstly with distilled water and then with alcohol.

Dry the cone.

Weigh, and note the weight.

The solution in the beaker may be tested for nickel by transferring, by means of a pipette, some of the clear solution to a test tube and adding sulphuretted hydrogen.

Dissolve the nickel from off the weighed cone and test with solution of sulphocyanide, estimating the iron, if present, by comparing with the colour of a measured solution of known percentage of iron, contained in a corresponding cylinder, to which solution of sulphocyanide, in sufficient quantity, has been added.

The standard solution of iron, for colour comparison, is made by dissolving 0.007 gramme of iron wire in hydrochloric acid and making up to 1 litre

with water. Every 10 c.c. will, therefore, contain nearly 0.00007 gramme of iron = 0.0001 gramme of Fe_2O_3 .

The necessary correction for co-precipitated iron is made as directed.

EXAMPLE—	Grammes.
Weight of cone + “metal” deposited, .	15.5211
Weight of cone before the action of the current,	15.5125
	<hr/> 0.0086
Deduct weight of Fe_2O_3 , . .	<hr/> 0.0003
Weight of nickel, . .	<hr/> <hr/> 0.0083

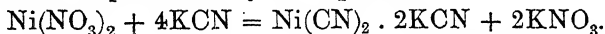
Then as 0.31 gramme had been taken,

$$\frac{0.0083 \times 100}{0.31} = 2.677.$$

2.68 \doteq percentage of nickel in the sample of steel.

VOLUMETRIC ESTIMATION OF NICKEL IN NICKEL STEEL.

Outline of the Process.—A weighed portion of the sample is dissolved in acid, and the solution is cooled. Potassium cyanide is added to keep the nickel in solution when the iron is precipitated on being poured into ammonia liquor. The precipitate is separated, and a definite quantity of the clear solution is withdrawn and treated with acid to decompose the cyanide. The solution is then made slightly alkaline, and a cloud of silver iodide is precipitated to act as an indicator. Standard solution of cyanide is now measured from a burette. The first effect is the formation of double cyanide of nickel and potash—a reaction represented by the equation—



The double cyanide and the potassium nitrate both remain in solution.

When the nickel present has been satisfied, the next drop of cyanide dissolves the cloud of silver iodide, thus indicating the end of the reaction.

The strength of the standard solution being known, it is easy to calculate, from the number of c.c. used, the quantity of nickel present.

Solutions required.

Silver nitrate,	0.5 gramme in 1 litre of water.
Potassium iodide,	20 grammes in 1 „
Potassium cyanide,	50 „ 1 „
and Standard potassium cyanide,	containing 4.44
grammes of pure KCN per litre.	

The equation on p. 173 shows that 58·7 parts by weight of Ni require 260·4 parts by weight of KCN

$$\frac{260\cdot4}{58\cdot7} = 4\cdot44.$$

To prepare the standard potassium cyanide solution, it is necessary in the first place to find the percentage of KCN in the "pure potassium cyanide" supplied or in stock. This is ascertained by dissolving a weighed quantity of the cyanide, and titrating with $\frac{N}{10}$ silver nitrate solution (16·99 grammes of pure silver nitrate dissolved in 1 litre of water).

When silver nitrate solution is added to potassium cyanide solution a double cyanide is formed—



The double cyanide is soluble, but, on the addition of one drop of silver nitrate in excess, a white permanent precipitate or cloud is formed.

1 c.c. of $\frac{N}{10}$ silver nitrate solution = 0·013049 gramme of KCN.

EXAMPLE.—Weighed off 1·0066 gramme of "pure" potassium cyanide, dissolved, and made up to 250 c.c. Mixed well.

Measured off 50 c.c. for titration.

This required 15·20 c.c. of $\frac{N}{10}$ silver nitrate solution. This was confirmed by a duplicate determination.

$$\text{Then } 15\cdot20 \times 0\cdot013049 \times \frac{250}{50} \times \frac{100}{1\cdot0066} = 98\cdot52.$$

98·52 = percentage of KCN in the cyanide.

Then for 1 litre containing 4.44 grammes of KCN,

$$\frac{4.44 \times 100}{98.52} = 4.5067$$

grammes of the "pure" cyanide will be required.

The standard solution of potassium cyanide was prepared accordingly, and, on titration with $\frac{N}{10}$ silver nitrate solution, was found to be correct, each c.c. of the standard solution containing 0.00444 gramme of KCN, which is equivalent to 0.001 gramme of nickel.

STANDARDISING THE CYANIDE SOLUTION.

0.3315 gramme of pure nickel wire was dissolved, the solution was cooled, diluted to 250 c.c., and 25 c.c. withdrawn for titration. 5 c.c. of the standard silver nitrate and 5 c.c. of the standard potassium iodide solutions were added, and the quantity of standard cyanide solution needed to clear the cloud was delivered from a burette.

The standard cyanide required was 32.5 c.c.

Weight of nickel in the portion of solution used for titration = 0.03315 gramme.

$$\frac{0.03315}{32.5} = 0.00102,$$

and 0.00102 = weight of nickel equal to each c.c. of the standard cyanide solution. This was confirmed by another estimation.

Copper—which is more readily obtained in a state of purity than nickel—may be used for standardising the cyanide solution.

EXAMPLE—

Weight of pure copper taken = 0.3151 gramme.

Copper in $\frac{1}{10}$ withdrawn . = 0.03151 "

Standard cyanide solution

required = 30.3 c.c.

$$\frac{0.03151}{30.3} = 0.00104.$$

Atomic weight of nickel = $\frac{58.7}{63.6} = 0.923$.

" " copper = $\frac{63.6}{63.6} = 1.0$.

$$0.00104 \times 0.923 = 0.0009599.$$

0.00096 = weight of nickel equal to each c.c. of the standard solution.

The cyanide solution for titrating may be standardised with steel containing a known percentage of nickel.

Details of the Process.—Weigh off a quantity of the sample, and note the weight taken. For steels containing under 1 per cent. of nickel use 2 grammes of sample; for richer samples use 1 gramme.

Transfer the weighed sample to a 400 c.c. beaker.

For 1 gramme add 25 c.c. of nitric acid of 1.2 specific gravity. [If the steel contains 0.7 per cent. or more of carbon, hydrochloric acid should be used as a solvent.]

Heat until the steel has dissolved and the evolution of nitrous fumes ceases.

When cool, add about 8 c.c. of a 5 per cent solution of potassium cyanide to keep the nickel in solution.

Wash the contents of the beaker into a 250 c.c. flask containing about 50 c.c. of ammonia liquor (sp. gr. 0.88) in 100 c.c. of water.

Make up to the mark with cold water.

Mix well.

Allow the precipitate of ferric hydrate to settle.

Filter about 100 c.c. through a dry filter into a spouted beaker.

Fill a clean 50 c.c. burette with the filtered solution, and run the liquid away.

Fill the burette to zero with more of the filtered solution.

Measure off 50 c.c. into a 350 c.c. (about 12-oz.) conical flask.

Add 15 c.c. of 1.42 specific gravity nitric acid.

Boil briskly for five minutes to destroy the double cyanide.

Neutralise with ammonia liquor and add 1 c.c. in excess.

Dilute to about 100 c.c. with cold water.

Add 5 c.c. of the silver nitrate solution and 2 c.c. of the potassium iodide solution. This causes a cloud of silver iodide, which acts as an indicator.

Fill a 30 c.c. burette with the standard cyanide solution and run the liquid away. This is done to clear the cleaning water out of the burette.

Fill the burette to zero with the standard cyanide solution.

Run standard cyanide solution from the burette into the 12-oz. conical flask—very cautiously and with occasional shaking of the flask towards the end—until the liquid becomes clear.

Note the quantity taken, allow for blank, and calculate the result.

EXAMPLE---

Sample weighed off. . . = 1 gramme.

$\frac{1}{2}$ taken for titration . . = 0.2 .,

Standard cyanide solution

required . . . = 6.04 c.c.

$$\frac{6.04 \times 0.00102 \times 100}{0.2} = 3.08.$$

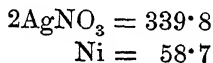
3.08 = percentage of nickel in the sample

RAPID VOLUMETRIC METHOD FOR THE ESTIMATION OF NICKEL IN STEEL.

With practice, good results may be obtained by this method. It is, therefore, useful for the estimation of nickel in furnace samples.

Outline of the Process.—A weighed portion of the sample is dissolved and neutralised. A measured amount of standard solution is added, and the iron is precipitated. On filtering and washing, the nickel is separated and is estimated by titrating with standard silver nitrate solution.

The reaction requires 2 equivalents of silver nitrate for each equivalent of nickel.



The solutions required for this method are—

Standard silver nitrate solution containing

$$\frac{339.8}{58.7} = 5.789 \text{ grammes in 1 litre of water.}$$

Standard potassium cyanide solution made up so that 1 c.c. equals 1 c.c. of the standard silver nitrate solution. For this purpose the standard cyanide solution should contain 4.44 grammes of KCN per litre.

This is prepared by first ascertaining, by titration with $\frac{N}{10}$ silver nitrate solution, the amount of KCN in

the cyanide by the method described on pp. 234 and 235, and then weighing off and dissolving the required amount of "pure" cyanide. For example of calculation, see p. 235.

Details of the Process.—Weigh off 1 gramme of the sample.

Transfer the weighed portion to an 800 c.c. beaker.

Add 10 c.c. of 1.2 specific gravity nitric acid, along with 1 c.c. of 1.16 specific gravity hydrochloric acid, and 5 c.c. of water.

Set on a hot plate to dissolve.

When dissolved, wash the solution into a 500 c.c. graduated flask.

Add about 150 c.c. of cold water.

Add dilute ammonia solution (1 of 0.880 specific gravity ammonia in 5 of water) cautiously, and with frequent vigorous shaking, until a slight permanent precipitate forms.

Measure from a burette 10 c.c. of the standard cyanide solution for every 1 per cent. of nickel expected. Measure also 10 c.c. in excess, and note the amount taken.

Shake the flask to mix the contents, and add about 30 c.c. of 0.880 specific gravity ammonia liquor.

Make up to 500 c.c. with cold water.

Shake the flask to mix the contents.

Filter through a dry 20 cm. thick filter. Collect the filtrate in a clean beaker, and stir well.

Measure off 250 c.c. of the filtrate into a flask of about 600 c.c. capacity.

Add glacial acetic acid until just neutral. Much

of the success of the estimation depends on the accuracy with which neutralisation is effected.

Add 6 drops of dilute ammonia (1 of 0.880 specific gravity ammonia in 5 of water).

Dissolve 2 grammes of ammonium sulphate in the solution in the flask. This serves the double purpose of increasing the iodine turbidity, and retards the formation of a deceptive precipitate which is not readily soluble in small excess of potassium cyanide.* It also retards the formation of a nickel-molybdenum precipitate, if the latter is present.

From a burette, measure standard silver nitrate solution. Shake the flask while adding the silver nitrate. Cautiously continue the additions till a white cloud is formed which remains even after shaking the solution.

Some analysts prefer to overshoot the mark by adding excess of the standard silver nitrate solution, and then adding enough of the standard cyanide to clear the solution.

EXAMPLE OF CALCULATION.—1 gramme of sample dissolved, half of the solution titrated.

50 c.c. of standard cyanide solution used.

5.1 c.c. of standard silver nitrate required to give milkiness or cloud.

Multiply the No. of c.c. of the standard silver solution used by 2, add 10 per cent., and divide by 10.

In this instance $5.1 \times 2 + 10$ per cent. = 11.22.

* Brearley and Jervis, *Chemical News*, 7th October, 1908.

Subtract from the No. of c.c. of standard cyanide used

$$50 - 11.22 = 38.78.$$

Now divide by 10: result, 3.88.

3.88 = percentage of nickel in the sample of steel.

ESTIMATION OF NICKEL IN FERRO-NICKEL.

The portion of the sample taken for the estimation of nickel should be reduced to the finest possible state of division in an agate mortar.

Weigh off very accurately about 0.25 gramme of the finely-pulverised sample, and proceed with the estimation as directed in the preceding pages—using less, but not proportionately less, acid, &c.

ESTIMATION OF COBALT.

Gravimetric method as recommended by the Chemists' Committee of the United States Steel Corporation.

Weigh off 2 grammes of the sample into a 400 c.c. beaker.

Add 50 c.c. of 1.16 specific gravity hydrochloric acid.

Heat gently until action ceases.

Add 10 c.c. of 1.2 specific gravity nitric acid, or 1 gramme of sodium chlorate.

Evaporate till the salts just begin to separate.

Dilute with water to ensure solution of all soluble salts, and transfer to a 500 c.c. graduated flask.

Add an emulsion of zinc oxide in excess, which is shown when the supernatant liquid becomes milky.

When cooled to about 15° C., dilute with water to the mark, mix well, and set the flask aside till the heavy precipitate has settled.

Filter off 250 c.c. into a graduated flask, and transfer to an 800 c.c. beaker.

Add about 7 c.c. of 1.16 specific gravity hydrochloric acid and about 100 c.c. of water.

Heat to boiling.

Precipitate the cobalt by adding a sufficient quantity of nitroso- β -naphthol solution. This solution is prepared by dissolving the compound in glacial acetic acid in the proportion of 1 gramme

in 10 to 15 c.c. of the acetic acid. A volume of the solution of the reagent equal to 1 gramme of the compound should be added for each 0.025 gramme of cobalt present.

Stir well, and allow the red-coloured precipitate to settle in a warm place.

Filter the hot solution.

Wash once with 1.16 specific gravity hydrochloric acid diluted with an equal bulk of water.

Wash once with water.

Wash once again with the diluted acid and nine or ten times with hot water.

Dry the precipitate.

Ignite the filter and precipitate in a tared porcelain crucible, at first gently until the carbonaceous matter has disappeared, and then at a high temperature for 20 minutes at least.

Allow to cool in a desiccator and weigh the residue of Co_3O_4 and filter ash.

Co_3O_4 contains 73.44 per cent. of cobalt.

VOLUMETRIC ESTIMATION OF COBALT AND NICKEL IN COBALT STEEL.

The process here given was worked out by W. R. SCHOELLER, Ph.D., and A. R. POWELL (London), and submitted to the meeting of the Iron and Steel Institute in May, 1918.

Outline of the Process.—The weighed sample is digested with strong acids, several hours' boiling with aqua regia being required to get the material into solution. The solution is then concentrated and a little sulphuric acid added. The iron is carefully precipitated by means of sodium carbonate and filtered off. From the filtrate the cobalt and nickel are precipitated (together with small quantities of iron, chromium, and manganese) by caustic soda. The precipitate is dissolved and tartaric acid is added to the solution, so as to prevent precipitation of iron and chromium. Strong ammonia solution is then added, followed by the addition of potassium iodide. The iodide causes the precipitation of all the cobalt and nickel, along with a little manganese. This is dissolved and reprecipitation of the cobalt is caused by the addition of ammonium phosphate solution. By titrating the filtrate with $N/5$ acid the amount of nickel is estimated. The precipitate of cobalt-ammonium-phosphate (containing a little manganese) is dissolved and titrated, a known proportion of the titrated solution is withdrawn, and the quantity of manganese in it is estimated.

Several assays can be completed in four hours from the time the steel has been obtained in solution.

Details of the Process.—Weigh off about 2 grammes of the sample, note the weight, and transfer the weighed portion to a 500 c.c. high-class beaker.

Add 30 c.c. of strong hydrochloric acid and 30 c.c. of strong nitric acid.

Heat gradually for half an hour, then boil gently for about five hours and evaporate almost to dryness.

When cool, add 2 c.c. of sulphuric acid (1 : 1), a little hydrochloric acid, and 25 c.c. of water.

Heat slowly until the residue is dissolved. The addition of the prescribed amount of sulphuric acid is essential for the success of the next operation, as it produces a pale brown pulverulent precipitate which is easily filtered off.

Cool the solution and dilute to 50 c.c. with cold water.

From a burette add 20 per cent. sodium carbonate solution. When the iron begins to come down withdraw a drop between the additions of carbonate and bring into contact with a drop of 10 per cent. thiocyanate solution in a flat porcelain basin used as a spot plate. When the red colouration grows faint and becomes masked by the rust-brown precipitate, wash the spot tests into a 200 c.c. graduated flask.

Wash the contents of the beaker into the same flask, and make up to the mark with water.

Filter the solution through a 12.5 cm. dry pleated filter.

Pipette 100 c.c. into a 300 c.c. beaker.

Add 2 c.c. of nitric acid, and boil.

Add 25 c.c. of bromine water.

Add an excess of freshly prepared caustic soda solution.

Boil for one or two minutes.

Filter the black precipitate through a Whatman's No. 4 9 cm. filter paper.

Wash well with boiling water.

The precipitate contains all the cobalt and nickel, together with small quantities of iron, chromium, and manganese.

Place the 300 c.c. beaker under the funnel, and, by means of a little hydrochloric acid, dissolve the precipitate and wash the whole into the beaker.

Evaporate the solution almost to dryness.

Add 2 c.c. of strong nitric acid, and again evaporate so as to destroy the bulk of the chlorides.

Add 1 gramme of tartaric acid in cold saturated solution, then add 50 to 60 c.c. of 0.88 specific gravity ammonia solution, followed immediately by a cold saturated solution of potassium iodide.

Allow the pale-pink crystalline precipitate, which is at once thrown down, to settle for about 15 minutes.

Filter through a 9 cm. filter.

From a wash-bottle fitted with a Bunsen valve wash the precipitate with a solution of 10 grammes of potassium iodide in 200 c.c. of 0.88 ammonia liquor and 50 c.c. of water.

Dissolve the iodide precipitate (which contains

only cobalt and nickel, with a little manganese) in 10 c.c. of hydrochloric acid and a little sodium sulphite solution poured through the filter collecting, the whole in a 300 c.c. beaker.

Finish the washing with hot water.

Add to the contents of the beaker 25 c.c. of a 5 per cent. ammonium phosphate solution.*

Heat the liquor to boiling.

Add 0.88 specific gravity ammonia solution diluted with an equal bulk of water drop by drop with continual stirring until the blue amorphous precipitate at first produced becomes pink and crystalline, then add five drops in excess.

Heat the assay on a steam bath for ten minutes.

Cobalt Titration.—Filter off the pink precipitate of cobalt-ammonium-phosphate through a 9 cm. filter paper.

Wash well with hot water. Collect the filtrate and washings in a beaker.

Spread the filter containing the washed precipitate against the sides of the beaker, in which precipitation was effected, and rinse with water followed by a few drops of N/5 sulphuric or nitric acid used in the titration, and again with water to displace the acid, taking care not to use more than 30 c.c. in all. Discard the filter and continue the gradual addition of acid until the precipitate

* This solution is prepared by dissolving the salt in hot water containing a few drops of methyl-orange solution, and adding hydrochloric acid till the colour turns pink. The whole should then be boiled for five minutes, allowed to cool, and filtered into a stock bottle.

disappears. No indicator is required, as the precipitate imparts a lilac colour to the liquid, and its final disappearance can be ascertained within 0.1 c.c.

Deduction for Manganese Present.—Filter the titrated liquid (to free it from filter fibres) into a 100 c.c. graduated flask.

Pipette 10 or 20 c.c., boil with persulphate and silver nitrate in the usual manner, and match against a standard solution containing 0.072 gramme of potassium permanganate per 500 c.c. (1 c.c. — 0.05 milligramme). One to three mgr. of manganese may be thus found. The acid consumed by the manganese-ammonium-phosphate (0.19 c.c. per mgr. of manganese) is subtracted from the volume found, the difference giving the cobalt (1 c.c. of N/5 acid = 0.0059 gramme of cobalt).

Nickel Titration.—Collect the filtrate from the cobalt-ammonium-phosphate in a conical flask.

When cool, titrate with a standardised solution containing 10 grammes of sodium cyanide, 2 grammes of caustic soda, and 1 gramme of silver nitrate per litre. The quantity of nickel being very small, the assay is left for a few minutes after about 1 c.c. of cyanide solution has been added, when the cloudiness due to silver iodide becomes visible. The addition of cyanide is then continued drop by drop, whilst shaking, until the liquid clears. The cyanide solution should be standardised every week against pure nickel or silver.

ESTIMATION OF ARSENIC.

METRIC ESTIMATION OF ARSENIC IN STEEL.—
HER'S PROCESS, AS APPLIED BY STEAD.*

In this process there are three stages :—

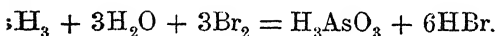
- (1) Dissolving the weighed sample.
- (2) Distilling the solution.
- (3) Titrating the distillate.

The following apparatus is employed, viz. :—

1). A 600 c.c. (about 20-oz.) conical flask with a tight rubber cork, carrying a safety funnel and a delivery tube, also a Winkler's absorption apparatus, as shown in Fig. 20, p. 252.

2). A distillation flask, Liebig condenser, and stands with tripod, as shown in Fig. 21,

Outline of the Process.—The weighed sample is transferred to the conical flask and dissolved in nitric acid. While dissolving, gaseous compounds are evolved, including some arsenuretted hydrogen (AsH_3), which is converted into arsenious acid (AsO_3), and absorbed in bromine water contained in the spiral of the Winkler absorption apparatus.



The excess bromine is boiled off, the remaining

* *Iron and Steel Institute Journal*, vol. i., 1895.

clear solution and the solution left in the flask (in which most of the arsenic has been re-precipitated) are washed into the distillation flask and distilled.

On prolonged distillation of the solution ferrous chloride of which assists the distillation

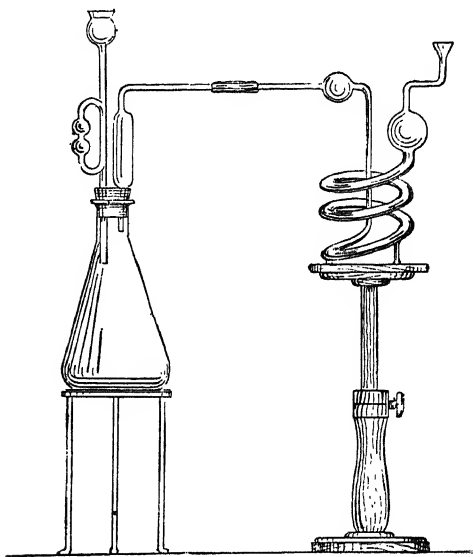
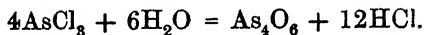
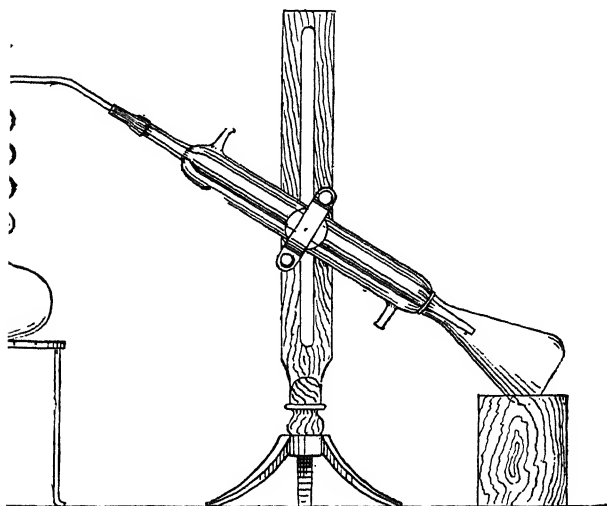
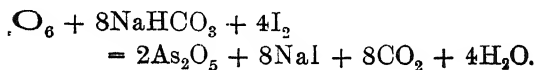


Fig. 20.—Apparatus used when dissolving steel containing arsenic. The arsenic is conveyed to the receiver as arsenic chloride (AsCl_3) which in excess of water is decomposed into arsenious oxide and hydrochloric acid thus—



The distillate is neutralised with ammonia.

alkaline by the addition of sodium bicarbonate, solution is added to act as an indicator, and arsenious oxide is titrated with standard iodine solution. The reaction may be represented by the following equation—



21.—Apparatus used when distilling the solution from arsenical steel.

ne, added in excess, strikes a blue colour with starch. From the quantity of standard iodine solution required to complete the reaction the amount of arsenic present is ascertained, and the percentage is calculated.

Details of the Process—Dissolving.—Weigh off 20 grammes of the sample, which should be in the form of fine turnings or drillings. (From 10 to 50 grammes may be weighed off.)

Transfer the weighed portion to the 20-oz. conical flask.

Moisten the rubber cork and press it tightly into the neck of the flask.

Set the flask on wire gauze over a burner.

Charge about one-third of the length of the spiral of the Winkler apparatus with saturated bromine water, and add about one c.c. of bromine. More bromine should be added if found to be required.

Bring the ends of the delivery tube and the Winkler apparatus close together, and slip the rubber connection into position.

Introduce through the safety funnel about 100 c.c. of water, and 120 c.c. of 1.16 specific gravity hydrochloric acid.

Heat the flask and contents so as to ensure the passage of a steady but not too rapid current of gas through the bromine solution. In the course of one hour the whole of the steel should be dissolved. When no more evolution of gas can be observed, boil the liquid in the flask so as to completely drive all the gas into and through the bromine solution.

Disconnect the Winkler apparatus and wash the solution into a 100 c.c. beaker.

Boil off the bromine.

Wash the clear solution into the distilling flask (Fig. 21).

Wash also the solution from the conical flask into

the distillation flask and close the neck with the stopper, or a tight-fitting cork.

Distilling.—Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter and place a 300 c.c. (about 10-oz.) conical flask in a position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

While distillation is proceeding the strength of the standard iodine solution may be ascertained (see pp. 261 and 262).

Gently distil till the liquid remaining in the flask is reduced to about 10 c.c. The distillation must not be forced; when finished, the distillate should be quite colourless and free from chloride of iron.

Add about 20 c.c. of 1.16 specific gravity hydrochloric acid to the contents of the distillation flask.

Again distil till the liquid remaining in the flask is reduced to about 10 c.c.

Add about 20 c.c. of 1.16 specific gravity hydrochloric acid, along with about 5 c.c. of water.

Distil till the liquid left in the distillation flask measures about 20 c.c. At this point, as a rule, all the arsenic will have passed into the distillate, but it is advisable to make quite certain and to add another 20 c.c. of 1.16 specific gravity hydrochloric acid, along with about 5 c.c. of water, and distil to very small bulk.

Remove the receiver and add to the (colourless)

distillate in it two or three drops of litmus solution, and then a slight excess of ammonia liquor.

Add a few drops of 1.16 specific gravity hydrochloric acid—to more than neutralise the ammonia and leave the solution faintly acid.

Add solid sodium bicarbonate (acid sodium carbonate) in slight excess.

Cool the contents of the flask.

Add about c.c. of clear, cold starch solution (see p. 344). Set the receiver on a white porcelain slab under the burette, and proceed with the titration as directed on pp. 259 to 263.

When dissolving steels in dilute hydrochloric acid, if there is no rust on the sample or ferric chloride present in the acid and the presence of air is carefully avoided, as a rule, only about one-tenth of the total arsenic passes off with the gas.

When solution is effected entirely in the cold a very much less quantity is evolved, and a very slight amount passes into the solution. As an example, an alloy containing 4.125 per cent. of arsenic dissolved in dilute hydrochloric acid in the cold gave the following results:—

Evolved as gas, .	.	0.035 per cent
Found in the solution, .	.	0.125 „
Remaining insoluble as a		
dense black residue, .	.	3.965 „
		<hr/>
		4.125 „

Alternative Method of Distilling.

The time occupied in distilling may be shortened by adopting the following modification:—

Transfer the weighed sample to the conical flask which has been fitted as shown in Fig. 20, p. 252.

Moisten the rubber cork and press it tightly into the neck of the flask.

Charge about one-third of the length of the spiral of the Winkler apparatus with saturated bromine water, and add about 1 c.c. of bromine.

Connect the Winkler apparatus to the delivery tube.

Introduce through the safety funnel about 100 c.c. of water and 120 c.c. of 1.16 specific gravity hydrochloric acid. This quantity should suffice for 25 grammes of sample.

Heat gently to hasten solution, and continue the heating till all the iron has been dissolved and only a little dark residue is left in the liquid in the flask.

Disconnect the apparatus.

Wash the bromine solution into a 250 c.c. beaker.

Boil off, gently, the bromine.

Wash the solution from the beaker into the conical flask.

Drop about half a gramme of zinc sulphide into the solution in the flask.

Shake the flask violently for about three minutes, so as to agitate the contents.

All the arsenic will then be in the insoluble state, partly as sulphide and partly as a black precipitate of, possibly, free arsenic and arsenide of iron.

Filter off through a 12.5 cm. smooth filter-paper. Rinse the flask with cold distilled water.

Wash the precipitate and residue two or three times with water, then wash the solids into a beaker of about 150 c.c. capacity. If the precipitate should happen to stick pertinaciously to the filter, dissolve with bromine water and hydrochloric acid, and wash the filter carefully with hot water to remove all traces of arsenic.

Dissolve the washed precipitate in bromine water to which a little hydrochloric acid has been added.

Boil off, gently, the bromine.

Wash the solution from the beaker into the distilling flask shown in Fig. 21, p. 253.

Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter and place a 300 c.c. (about 10-oz.) conical flask containing about 75 c.c. of water in position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

Add about 15 grammes of solid ferrous chloride, or about 5 c.c. of the steel solution remaining after separating the arsenic during a previous estimation. The solution should contain about 10 per cent. of soluble iron as ferrous chloride.

Close the neck of the distillation flask with the stopper or a tight-fitting cork.

Distil gently. Continue the distillation till the mixture in the flask is almost dry.

When the flask has cooled, add 20 c.c. of 1.16 specific gravity hydrochloric acid and distil again.

Add 20 c.c. of 1.16 specific gravity hydrochloric acid and 5 c.c. of 10 per cent. ferrous chloride, and again evaporate to small bulk.

While distillation is proceeding the strength of the standard iodine solution may be ascertained (see pp. 261 and 262).

Detach the distillation flask and wash the condenser out twice with water—First distillate.

To ensure the complete removal of the arsenic, pour 20 c.c. of 1.16 specific gravity hydrochloric acid into the distilling flask, connect the condenser, place a receiver in position, and distil again—Second distillate.

Remove the receiver. Add to the (colourless) distillate in the first receiver two or three drops of litmus solution and then a slight excess of ammonia liquor.

Add a few drops of 1.16 specific gravity hydrochloric acid—to more than neutralise the ammonia and leave the solution faintly acid.

Add solid sodium bicarbonate (acid sodium carbonate) in slight excess.

Cool the contents of the flask.

Add about 5 c.c. of clear, cold starch solution (see p. 344), and set the receiver on a white porcelain slab under the burette and proceed with the titration as directed.

Titration.—Fill a clean burette with standard iodine solution for arsenic estimation (see p. 341), and run off the solution into a sink.

Nearly fill the burette with the standard iodine

solution, place an Erdmann's float in the burette and adjust to zero.

Measure the standard iodine solution into the flask containing the distillate. Shake vigorously during addition. Continue the additions till a permanent violet or blue colouration is produced.

Read off and note the quantity of standard iodine solution required.

Treat the distillate from the second receiver in the same manner, and add the result, if any.

A "blank" is carried out side by side with tests in exactly the same way from the commencement, using the same quantity of acids and reagents.

From the quantity of standard iodine solution required, deduct the correction for the "blank," and calculate the percentage of arsenic found.

The iodine solution should be carefully standardised, and restandardised frequently.

EXAMPLE OF CALCULATION.—20 grammes of sample were taken for the estimation, and, after making the correction for the "blank," 16.4 c.c. of the standard iodine solution (each c.c. of which = 0.000498 gramme of arsenic) were required to complete the reaction.

$$16.4 \times 0.000498 = 0.00817.$$

0.00817 gramme = weight of arsenic in 20 grammes of the sample.

To find percentage—

$$\frac{0.00817 \times 100}{20} = 0.00817 \times 5 = 0.041.$$

0.041 = percentage of arsenic in the sample of steel.

STANDARDISING THE IODINE SOLUTION FOR ESTIMATION OF ARSENIC.

The standard solution of pure arsenious oxide (prepared as directed on p. 339) is assumed to contain 0.0005 gramme of arsenic per c.c., and is used to find the strength of the standard iodine solution as prepared for the estimation of arsenic.

Fill a clean burette with standard solution of arsenious oxide and run off the solution into a sink.

Refill the burette and adjust the solution to zero.

Measure 30 c.c. of the solution into an 18 cm. (about 7-inch) porcelain basin, or into a suitable conical flask.

Add about 100 c.c. of water, a few drops of litmus solution, an excess of sodium bicarbonate, and about 5 c.c. of freshly-prepared but cold starch solution (see p. 344).

Fill a clean burette with standard iodine solution for arsenic estimation (see p. 341), and run off the solution into a sink. Nearly refill the burette, place an Erdmann's float in the solution, and adjust to zero.

Measure the standard iodine solution into the solution in the basin or the flask (stirring or shaking

the contents meanwhile) until a somewhat persistent violet colour appears, then add it carefully drop by drop (stirring or shaking after each addition) until a distinct violet colour remains for about a minute after one of the drops.

Read off and note the volume, less the correction or blank (see p. 263) of iodine solution used.

Estimate the amount of standard iodine solution required for 35 c.c. of the standard arsenious solution, note the result, less the blank, and compare with the previous titration. If the results are not fairly concordant titrate again, using 25 c.c. of the standard arsenious solution. When three good consecutive results have been obtained the mean may be accepted.

EXAMPLE :—

Standard Arsenious Solution.	Standard Iodine Solution.	Iodine Solution Equal to Arsenious Solution.
c.c. 30	c.c. 30·2	c.c. 1·0067
35	35·1	1·0029
25	25·2	1·0080
		Mean 1·0059

Then as each c.c. of the arsenious solution contained 0·0066 gramme of arsenious oxide (= 0·0005 gramme of arsenic), the value of each c.c. of the standard iodine solution was $\frac{0·0005}{1·0059} = 0·000497$ gramme of arsenic.

The date of standardising, strength of the solution and amount allowed for blank should be noted on a label on the bottle containing the standard solution. Such a solution should be kept in a dark cupboard.

Correction for Quantity of Standard Iodine Solution required to show Colour in the Solutions used.

In a 300 c.c. conical flask dissolve about 0.5 gramme of sodium bicarbonate in about 200 c.c. of water, and add about 5 c.c. of freshly prepared but cold starch solution (see p. 344).

Set the flask on a white porcelain slab or piece of filter-paper under the burette containing the standard iodine solution.

Measure, from the burette—stirring vigorously after the addition of each drop—standard iodine solution until a distinct violet colour appears and remains. The depth of colour should correspond to that usually found at the end of an ordinary titration. The amount of the blank should be deducted from the reading of the burette when standardising and when assaying.

PLATTEN'S METHOD.

"This method was described by Mr. Platten in a paper read before the Society of Chemical Industry on 16th April, 1894, and depends on the fact that when sulphide of arsenic (obtained by treating the arsenical distillate with sulphuretted hydrogen) is boiled with

pure water, it is decomposed into sulphuretted hydrogen, which escapes, and arsenious oxide, which remains in solution. This solution is then titrated with iodine in the usual way."

"If the steel or iron contains much arsenic, a smaller quantity, say 1 or 2 grammes, may be dissolved in nitric acid of 1.20 specific gravity and the solution evaporated to dryness, the residue being dissolved in hydrochloric acid, and the solution transferred to the retort, and distilled directly with ferrous chloride and hydrochloric acid, care being taken that the distillation is not forced, so as to avoid any of the iron solution passing over into the distillate." *

GRAVIMETRIC METHOD FOR THE ESTIMATION OF ARSENIC IN STEEL.

Weigh off 10 grammes of the sample.

Transfer the weighed portion to a 15 cm. (about 6-inch) porcelain basin.

Add 50 c.c. of 1.42 specific gravity nitric acid, along with 30 c.c. of water.

Evaporate to dryness and roast thoroughly.

Allow to cool.

Detach as much as possible of the roasted mass and transfer it to a distilling flask (Fig. 20, p. 185).

Add 100 c.c. of 1.16 specific gravity hydrochloric acid.

Add about 25 grammes of solid ferrous chloride.

Dissolve the residue on the basin by adding 25

* *Stead. Iron and Steel Institute Journal*, vol. ii., 1895

c.c. of 1.16 specific gravity hydrochloric acid, and boiling.

Pour the solution into the flask.

Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter, and place a 300 c.c. (about 10-oz.) conical flask containing about 75 c.c. of water in position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

Distil gently. Continue the distillation till the mixture in the flask is almost dry. If the distillation has not been forced the distillate will be quite colourless.

Detach the distillation flask and wash the condenser out twice with water.

Remove the receiver and add to the distillate in it just enough ammonia liquor to make it neutral.

Acidify slightly but distinctly with hydrochloric acid.

Heat to 44° C.

Pass a current of sulphuretted hydrogen through the liquid for about twenty minutes.

Add about half a gramme of zinc sulphide to the solution.

Shake the flask vigorously for about three or four minutes.

Collect the precipitate on an 11 cm. Swedish or black ribbon filter.

Wash three times with cold water. Wash the precipitate down to the bottom of the filter.

Take away the beaker containing the filtrate and washings and place a 500 c.c. beaker under the funnel.

Pierce the filter, and with a warm solution of ammonia (1 of 0.88 specific gravity ammonia to 4 of water) wash the precipitate into the beaker.

Evaporate to one-fourth the bulk.

Add an equal bulk of nitric acid.

Again evaporate to small bulk.

Allow to cool.

Neutralise by adding ammonia liquor.

Filter, if necessary, into a 250 c.c. conical flask.

To the clear, warm liquid add, drop by drop, 10 c.c. of magnesia mixture (see p. 167).

Add 20 c.c. of 0.88 specific gravity ammonia liquor.

Cork the flask and shake it vigorously for two or three minutes. This should cause the precipitation of all the arsenic in the form of magnesium-ammonium arsenate $[\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}]$.

When the precipitate has settled, filter into a 9 cm. Swedish filter.

Wash six or seven times with ammonia water—say 1 of 0.88 specific gravity ammonia liquor to 4 of water.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Open out the dried filter and detach as much as possible of the precipitate.

Transfer the precipitate to a tared porcelain crucible.

Place the filter-paper in another tared porcelain crucible, saturate the paper with strong ammonium nitrate solution; dry and ignite the paper, gently at first, and finishing in a muffle which is at a red heat. These precautions are taken to avoid reduction and volatilisation of arsenic.

Set the tared crucible containing the precipitate over a good Bunsen burner. By means of an ordinary tobacco pipe, the inverted bowl of which covers the crucible, convey a slow current of oxygen to the crucible. Gradually raise the temperature to bright redness. Continue the heating in an atmosphere of oxygen for ten minutes after the highest temperature has been attained. By careful ignition in an atmosphere of oxygen a residue of fixed composition may be obtained.

During ignition, the precipitate loses ammonia and water, and is converted into magnesium-pyroarsenate, $\text{Mg}_2\text{As}_2\text{O}_7$, thus—



Allow the crucibles to cool in a desiccator, weigh, and note the weight.

Repeat the heating of the crucible which contained the precipitate in an atmosphere of oxygen.

Allow to cool in a desiccator.

Reweight.

Repeat the ignition in oxygen, if necessary, until the weight becomes constant.

Calculate the percentage.

EXAMPLE—

Weight of crucibles + ash	.	=	19.3819	grammes.
„ crucibles	.	=	19.3767	„
„ ash and precipitate	.	=	0.0052	gramme.
„ filter ash	.	=	0.0008	„
„ precipitate ($Mg_2As_2O_7$)		=	0.0044	„

The percentage of arsenic is calculated from the weight of pyroarsenate, which contains 48.272 per cent. of arsenic.

When 10 grammes of sample are operated on, the factor for ascertaining the percentage is—

$$\frac{48.272}{10} = 4.8272.$$

$$\text{Log } 4.8272 = 0.6836953.$$

$0.0044 \times 4.8272 = 0.021$ = percentage of arsenic in the sample of steel.

ESTIMATION OF ARSENIC IN PIG IRON.

“In testing pig irons they may be dissolved in nitric acid and evaporated to dryness, or be treated in a flask with hydrochloric acid, as previously described, but if the latter method is adopted, it is advisable to distil without separating the arsenic as sulphide in the first instance.” *

The gravimetric method described in the foregoing pages is also applicable to pig irons.

* Stead, *Iron and Steel Institute Journal*, vol. i., 1895.

ESTIMATION OF ARSENIC IN IRON ORES.

"In testing ores it is only necessary to place the ore directly into the retort, and distil at once with hydrochloric acid and ferrous chloride, taking care to place a few pieces of firebrick in the vessel, to avoid the 'jumping' of the liquid.

"If the ore contains much peroxide of manganese, it is advisable to dissolve it in a separate vessel to liberate and expel the chlorine, and then to transfer it into the retort.

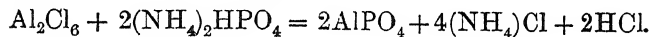
"It is quite possible to accurately determine as small a quantity as 0.002 per cent. arsenic by this method." *

* Stead, *Iron and Steel Institute Journal*, vol. i., 1895

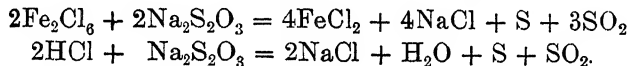
ESTIMATION OF ALUMINIUM.

ESTIMATION OF ALUMINIUM IN STEEL.

Outline of the Process.—The weighed sample is dissolved in hydrochloric acid, the solution is evaporated to dryness, re-dissolved, and the silica separated. Ammonium phosphate is added to the solution, and a reaction takes place which may be represented by the equation—



Sufficient ammonia liquor is then added to nearly neutralise the acid, and excess of sodium thiosulphate is added to reduce the iron to the ferrous condition and complete the neutralisation of the acid, thus—



At this stage—the solution being neutral—all the aluminium is precipitated as phosphate on boiling. As this is accompanied by a small amount of ferric phosphate, the precipitate is collected on a filter, washed, and dissolved. The iron is precipitated by excess of sodium hydrate, and separated from the soluble aluminate of soda by fractional filtration.

From the filtrate the aluminium is again precipitated as phosphate, which is collected, washed, dried, ignited, and weighed. The percentage is then calculated.

NOTE.—The precipitates should be rapidly filtered as soon as ready, and quickly washed.

Details of the Process.—Weigh off a quantity of fine drillings, and note the weight taken. If the steel is supposed to contain about 0.01 per cent. of aluminium, 11 grammes of the sample may be weighed off.

Transfer the weighed drillings to a 600 c.c. broad Bohemian or Jena beaker.

Add 50 c.c. of 1.16 specific gravity hydrochloric acid.

Heat on a hot plate (see note on p. 149) till dissolved, and evaporate to dryness.

Add hydrochloric acid and hot water to the residue, and boil to dissolve the iron, &c.

If an insoluble residue (silica, &c.) is present, filter through a 12.5 cm. Swedish filter, and wash with a fine jet of water, collecting the filtrate and washings (which should not exceed 200 c.c.) in a 500 c.c. beaker.

Boil.

To separate the aluminium phosphate from the main bulk of the iron:

Add sufficient ammonium phosphate solution to precipitate all the alumina present at a subsequent stage of the estimation. 0.5 c.c. of 20 per cent. solution (or 5 c.c. of 2 per cent. solution) will precipitate all the alumina from 11 grammes of a sample containing not more than 0.07 per cent. of aluminium. If more aluminium than this is likely to be present a proportionately greater volume of phosphate solution must be added. But the phosphate must not be greatly in excess of the amount required to precipitate the aluminium, or too much ferric phosphate will be thrown down with it.

Add dilute ammonia solution till the free acid is neutralised. This point is readily known by a small precipitate of phosphates remaining insoluble after repeatedly shaking the solution.

Add hydrochloric acid, drop by drop, till the solution is clear.

Boil.

As soon as boiling commences add 50 c.c. of boiling saturated solution of sodium thiosulphate (see p. 344).

Continue the boiling till the solution does not give off sulphurous anhydride. If there is a doubt whether or not there is excess of thiosulphate, add a few more c.c. of the saturated solution, and if this does not give a precipitate of sulphur, sufficient thiosulphate has been added.

Test for sulphurous anhydride by holding a piece of filter-paper moistened with solution of dichromate or permanganate of potash in the vapour from the beaker.

While the solution is still very hot, filter the precipitate into a fluted 12.5 cm. Swedish filter, collecting the filtrate (and washings) in a 600 c.c. beaker.

Rinse out, with hot water, the beaker in which the precipitate was formed, but do not trouble to detach any firmly-adhering precipitate at this stage.

Wash the precipitate on the filter with hot water till free from all soluble iron and other salts. If the filtrate is slightly turbid on account of the presence of sulphur, the turbidity may be neglected.

Allow the precipitate to drain and then remove the beaker. The filtrate and washings are of no further use.

To separate the co-precipitated ferric hydrate :

Place a clean 400 c.c. beaker under the filter.

Warm 10 c.c. of 1.16 specific gravity hydrochloric acid, and 10 c.c. of water in the beaker in which the precipitation was effected, and pour the solution into the filter.

With a fine spout wash bottle wash with warm dilute hydrochloric acid (1 of 1.16 sp. gr. acid to 3 of water) till the whole of the phosphates are dissolved, and only a residue of sulphur is left on the paper. Wash again with the acid water and twice with hot water.

Evaporate the solution to a low bulk, and then transfer to a 7.5 cm. (about 3-inch) platinum or silver basin.

Place the basin over a water bath and evaporate to dryness.

Add about 3 grammes of pure sodium hydrate (caustic soda) prepared from sodium, and about 1 c.c. of hot water to partially dissolve it.

Heat gently over a Bunsen burner till evaporated to dryness, and afterwards more strongly till in a state of tranquil fusion.

Allow the basin and contents to cool.

Add about 50 c.c. of hot water, boil for about five minutes and allow to cool.

Transfer the liquid (containing soluble aluminate of soda and a precipitate of ferric hydrate) to a 110 c.c. graduated flask or measure.

Make up to the mark with cold water.

Mix the liquids well.

Pour into a dry double 12.5 cm. Swedish filter,

collecting 100 c.c. of the filtrate in a graduated flask. If the filtrate is turbid or cloudy it should be re-filtered.

Transfer the 100 c.c. of clear, filtered liquid to a 600 c.c. beaker.

To precipitate pure aluminium phosphate :

Add 4 c.c. of 20 per cent. ammonium phosphate solution.

Add dilute hydrochloric acid, little by little, till the precipitate which forms redissolves.

Make up with water to about 250 c.c.

Boil. As soon as the boiling commences add 25 c.c. of boiling saturated solution of sodium thiosulphate (see p. 344).

Boil for about half an hour. If the beaker bumps badly, it is advisable to pass in a stream of air while boiling.

Allow the precipitate to settle.

Decant off the clear liquid through a 15 cm. Swedish filter into a large clean beaker

Add about 300 c.c. of boiling water to the precipitate in the beaker, allow to settle and again decant. This decantation should be performed at least three or four times, as the precipitate is difficult to wash.

Add more boiling water, and boil the large bulk of liquid before finally decanting through a 15 cm. Swedish filter.

Wash, with hot water, the precipitate into the filter.

Wash the precipitate in the filter with hot water, until the washings are free from chlorides.

Dry the precipitate by placing the funnel with

filter-paper and contents on a filter dryer (fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-papers in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents, and allow to cool in a desiccator.

Weigh quickly and note the weight.

Calculate the percentage.

EXAMPLE—

	Grammes.
Weight of crucible + ash + precipitate	= 10.0447
„ crucible	= 10.0384
„ ash + precipitate	= 0.0063
„ filter ash	= 0.0008
„ precipitate (AlPO_4)	= 0.0055

The washed and ignited precipitate consisting of AlPO_4 , contains 22.195 per cent. of aluminium.

$$\text{Log } 22.195 = 1.3462551.$$

Solution from 10 grammes was taken for the estimation.

$$\frac{0.0055 \times 22.195}{10} = 0.012,$$

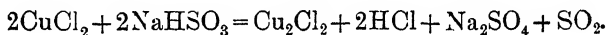
0.012 = percentage of aluminium in the sample of steel.

Aluminium in pig iron may be estimated by the above method.

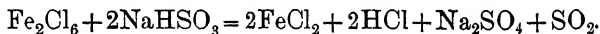
ESTIMATION OF COPPER IN STEEL.

GRAVIMETRIC ESTIMATION AS SULPHOCYANIDE OF
COPPER (BASED ON GUYARD'S METHOD).

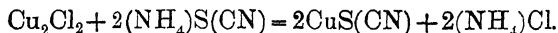
Outline of the Process.—A weighed portion of the sample is dissolved, the excess acids are neutralised, and hydrochloric acid is added. Alkaline bisulphite is then added to reduce the copper to the cuprous state—



Incidentally ferric chloride is reduced to ferrous chloride—



Ammonium thiocyanate (sulphocyanide) is added, and the copper present is precipitated as cuprous thiocyanate—



This precipitate is collected, washed, dried and weighed. The percentage is then calculated.

Details of the Process.—Weigh off 10 grammes of the sample and transfer to a 500 c.c. beaker.

Dissolve in the minimum amount of aqua regia (see p. 164), and boil off excess of acids.

Add sufficient ammonia liquor to cause the formation of a permanent precipitate.

Add 20 c.c. of 1.16 specific gravity hydrochloric acid

Dilute to about 400 c.c. with water.

Reduce the copper (and incidentally the iron present) by means of a strong solution of sodium bisulphite.

Heat to about 60° C.

Add 5 c.c. of a 10 per cent. solution of ammonium thiocyanate. This will cause the formation of a white precipitate of cuprous thiocyanate $[\text{CuS}(\text{CN})]$ if copper is present—with perhaps a little sulphur.

Collect the precipitate on a 12.5 cm. Swedish filter, and wash well with warm water.

Take away the beaker containing the filtrate and washings, and place a 400 c.c. beaker in its place.

With a solution of one part of 0.88 specific gravity liquor ammonia to two parts of water dissolve the thiocyanate on the filter.

Wash well with more ammonia water.

Acidify the contents of the beaker with hydrochloric acid, then add about 2 c.c. more of the acid.

Heat to about 60° C.

Add about 2 c.c. of 10 per cent. thiocyanate solution.

Allow the precipitate to settle.

Collect on a 9 cm. smooth filter.

Wash well with warm water.

Wash the precipitate into a 7.5 cm. (about 3-inch) tared basin.

Allow to dry on a water bath.

Wipe the outside of the basin with a cloth which does not leave fluff.

Allow to cool in a desiccator.

Weigh, and calculate the percentage.

EXAMPLE—

	Grammes.
Weight of basin + precipitate	23.4678
„ basin only	23.4625
„ precipitate	<u>0.0053</u>

The washed and dried precipitate contains 52.28 per cent. of copper, and when 10 grammes of sample have been taken for the estimation the factor for calculating is 5.228.

$$\text{Log } 5.228 = 0.7183356.$$

$0.0053 \times 5.228 = 0.0277$ = percentage of copper in the sample of steel.

Mr. John E. Stead gives * the following method:—

The alloy was dissolved in the least possible quantity to effect solution of nitro-hydrochloric acid, and when this was complete the solvent acids were removed by heating with strong sulphuric acid. The copper was separated by hydric sulphide, and the iron determined in the filtrate by a standard bichrome solution. The sulphides were dissolved in nitric acid, and the copper determined volumetrically by the iodine method, a method which has been found by long experience to give quite as accurate results as the most refined electrolytic methods.

* *Iron and Steel Institute Journal*, 1901, II., p. 110.

ESTIMATION OF TUNGSTEN IN STEEL.

Outline of the Process.—The weighed portion of the sample is treated with acids to effect decomposition. On continued heating, followed by dilution, tungstic oxide, accompanied by a little silica and ferric oxide, separates out. The solids are washed on a filter, dried, ignited, and weighed. The silica is carried off on treatment with hydrofluoric acid, the residue is fused with sodium carbonate, and the resulting sodium tungstate is dissolved and separated by filtering and washing. The dried insoluble residue is weighed. From the difference shown by the weighings the amount of tungstic oxide is ascertained, and the percentage of tungsten is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to an 11.5×10 cm. (about $4\frac{1}{2} \times 4$ inches) Bohemian or Jena beaker.

Add 50 c.c. of 1.16 specific gravity hydrochloric acid.

Cover the beaker with a clock glass, and heat nearly to boiling.

Add, not more than three or four drops at a time, 1.42 specific gravity nitric acid, allowing the frothing to subside completely before a further quantity is added. By the use of such a large excess of hydrochloric acid (which, although hot, is kept as concentrated as possible) the steel may be decomposed

by adding very little more nitric acid than is necessary to oxidise the iron without causing (and this is important) any separation of tungstic oxide. When complete decomposition has been effected, the iron should be in the ferric condition, and a black film of carbonaceous matter will have separated.

When decomposition has been completed, boil the liquid briskly to about one-third of its bulk. During the boiling a considerable amount of the tungstic oxide should separate out.

In the event of separation of tungstic oxide before complete decomposition of the drillings has been effected, the latter are protected from the attack of the acids, and the amount of the impurity in the separated residue is very much larger than is desirable.

Dilute with about 60 c.c. of hot distilled water.

Boil for a minute or two.

Filter, using a 12.5 cm. Swedish filter.

After transferring the tungstic oxide, so far as possible, to the filter, it will be found that in every case a film remains on the side of the beaker which defies removal by a "policeman." A small piece of ashless filter-paper, soaked with a drop or two of ammonium hydrate, readily brings it away, and the filter-paper is then ignited along with the main residue.

Wash the precipitate on the filter several times with hot water slightly acidulated with hydrochloric acid.

Place the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), cover with paper, and allow to dry on a hot plate.

Place the filter-paper with the dried residue in a platinum capsule, and ignite in a muffle furnace or over a Bunsen burner.

After ignition, add a few drops of pure hydrofluoric acid and a drop of sulphuric acid.

Cautiously remove the acid by evaporation and then heat the capsule and contents at a full red heat for a few minutes. This treatment eliminates the silica as (gaseous) silicon tetra-fluoride (SiF_4).

Allow the capsule and residue to cool.

Weigh, and note the weight of the capsule and contents.

Cover the powder in the capsule with 2 or 3 grammes of dry sodium carbonate, and place in a muffle furnace.

When complete fusion has taken place, withdraw the capsule, agitate it so as to mix the contents, allow to cool, add about 50 c.c. of water, and boil gently for a few minutes. The tungstic oxide will be dissolved.

Filter, using a 12.5 cm. Swedish filter. Collect the filtrate (and washings) in a beaker; if yellow, estimate the chromium present, as directed on p. 207.

Wash the residue on the filter several times with warm water.

Place the funnel with the filter-paper and washed residue (ferric oxide) on a filter dryer, cover with paper, and allow to dry on the hot plate.

Place the dried residue and filter-paper in the platinum capsule which had been used for the previous ignition, and ignite in a muffle furnace or over a Bunsen burner.

Allow to cool.

Weigh the capsule and residue, and note the weight.

The difference between the first and second weighings gives the weight of the tungstic oxide (WO_3).

Calculate the percentage.

EXAMPLE—

	Grammes.
Weight of capsule + tungstic oxide + ferric oxide, &c.	= 17.4895
After dissolving the tungsten compound— weight of capsule + ferric oxide, &c. + filter ash	= 17.1222
Weight of tungstic oxide	<u><u>0.3673</u></u>

Tungstic oxide (WO_3) contains 79.31 per cent. of tungsten, and when 2 grammes of sample are taken for the estimation the factor for calculation is—

$$\frac{79.31}{2} = 39.655.$$

$$\text{Log } 39.655 = 1.5982980.$$

$0.3673 \times 39.655 = 14.57 = \text{percentage of tungsten in the sample.}$

The filtrate and washings collected after the fusion with sodium carbonate contain the whole of the tungsten as sodium tungstate, and (if yellow) small quantities of chromium as sodium chromate. A very large number of assays by Ibbotson convinced him

that the determination of the chromium in the tungstic oxide residue may, for all practical purposes, be neglected, as its amount very nearly counterbalances the 2 or 3 milligrammes of tungstic oxide left in the solution when the evaporation of the original solution of the steel is not conducted far beyond the point at which tungstic oxide first falls out. If, however, it be considered necessary to determine the amount of the latter, the filtrate is acidulated with sulphuric acid, a slight excess (5 to 10 c.c.) of decinormal ferrous ammonium sulphate solution is added, and the excess of the latter titrated. The amount of chromic oxide found is deducted from the weight of the tungstic oxide.

ESTIMATION OF VANADIUM IN STEEL—VOLUMETRIC METHOD.

From a Memo. by J. KENT SMITH, American Vanadium Co.,
Pittsburg, Pa., U.S.A.

Mr. J. Kent Smith has investigated very fully the general methods for estimating vanadium in steels, &c. Those generally published are utterly unfit for works use, and often prove that they are not as correct as they should be. He has devised many methods based on the well-known reactions of vanadium and checked them synthetically in various ways. He claims no originality for either of the methods, which are based on the simplest laws of common-sense analysis, but they are giving very satisfactory results, and have stood comparison with many elaborate methods.

Details of the Process.—Weigh off 4 grammes of the steel, and dissolve in 48 c.c. of water and 12 c.c. of strong sulphuric acid.

When dissolved, oxidise with nitric acid, not using a great excess.

Evaporate to dryness on a hot plate.

Take up with 150 c.c. of water, and boil till dissolved.

Add 10 c.c. (or excess) of a $2\frac{1}{2}$ per cent. permanganate solution, and boil for five minutes.

Add a little manganese sulphate to precipitate any undecomposed permanganate.

Cool, and make up to half a litre with water.

Filter through a dry paper and take 375 c.c. of the clear filtrate (equals 3 grammes of steel).

Add 50 c.c. of dilute sulphuric acid.

Add a measured excess of $\frac{N}{10}$ ferrous sulphate (20 c.c. is enough for a steel containing $1\frac{1}{4}$ per cent. chromium), and titrate back with $\frac{N}{10}$ permanganate till permanently pink.

The equivalent of $\frac{N}{10}$ permanganate used up equals chromium (1 c.c. = 0.001743 gramme of chromium).

Now add 1 or 2 c.c. of ferrous sulphate solution to dissolve any MnO_2 that may have been formed, and add permanganate *very gradually* until the solution is just pink. Just discharge this pink with $\frac{N}{20}$ ferrous sulphate.

NOTE.—On the exact carrying out of this manipulation depends the accuracy of the vanadium estimation. With a little practice a fair manipulator should have no difficulty in hitting the point to a drop.

Next add a carefully measured 5 c.c. or excess of $\frac{N}{20}$ ferrous sulphate, and titrate back with $\frac{N}{20}$ dichromate solution and ferricyanide.

The equivalent quantity of dichromate used up equals vanadium (1 c.c. $\frac{N}{20}$ dichromate = 0.00256 gramme vanadium).

EXAMPLES OF CALCULATION—

CHROMIUM.

20 c.c. ferrous sulphate used (approximately $\frac{N}{10}$).

Original ferrous sulphate 20 c.c. = 21.2 c.c. $\frac{N}{10}$ $KMnO_4$.
 $\frac{N}{10}$ $KMnO_4$ to bring back . . . = 5.6 c.c.

Equivalent of $\frac{N}{20}$ $KMnO_4$ to
 chromium = 15.6 c.c.

$$\frac{15.6 \times .001743 \times 100}{3} = 0.906 \text{ per cent. Cr.}$$

VANADIUM.

5 c.c. ferrous sulphate used (approximately $\frac{N}{20}$).

Original FeSO_4 used . . . = 5.4 c.c. $\frac{N}{20}$ dichromate.

$\frac{N}{20}$ $\text{K}_2\text{Cr}_2\text{O}_7$ to bring back . . . = 3.0 c.c.

Equivalent of $\frac{N}{20}$ $\text{K}_2\text{Cr}_2\text{O}_7$ to
vanadium = 2.4 c.c.

$$\frac{2.4 \times .00256 \times 100}{3} = 0.204 \text{ per cent. vanadium.}$$

ESTIMATION OF VANADIUM IN ORES AND ALLOYS.

VOLUMETRIC METHOD.

Take 0.512 gramme of the finely powdered sample, and, in the first case, dissolve in dilute nitric acid, in the second in aqua regia, digesting in a warm place only.

To the solution add excess of strong sulphuric acid, and evaporate till copious fumes are evolved.

Dilute the liquid with water at about 30° C.

Add permanganate till just pink, and the "neutral" point has been attained as before.

Add a measured excess of $\frac{N}{10}$ ferrous sulphate, and titrate the excess with $\frac{N}{10}$ dichromate (1 c.c. = .00512 gramme vanadium).

The equivalent c.c. of $\frac{N}{10}$ dichromate due to vanadium represents the percentage of vanadium.

EXAMPLE—

0.512 gramme alloy used.

FeSO₄ added.

50 c.c. . . = 51.7 c.c. standard $\frac{N}{10}$ K₂Cr₂O₇.

Excess FeSO₄ . . = 12.5 " "

Vanadium equivalent, 39.2 " "

= 39.20 per cent. vanadium.

N.B.—In oxides, &c., the vanadium percentage divided by 0.5614 equals the percentage of V₂O₅.

NOTES.—In the cases of ores and alloys difficultly soluble, a very convenient way to bring the vanadium into solution is to fuse the ore or alloy in a nickel or iron crucible with about eight times its weight of sodium peroxide, dissolving the melt in water, boiling, acidifying with sulphuric acid, and proceeding as usual.

Difficultly soluble alloys may also be readily dissolved by covering the finely floured alloy in a platinum dish with 15 c.c. HNO₃ (1.2 sp. gr.), and 20 c.c. dilute H₂SO₄ (1 to 3), letting as much as will dissolve on heating, and then adding about 2 c.c. of HF, and smoking off to sulphuric fumes. The solution is diluted, "neutralised," and titrated as usual.

The clarity of the end reaction is much enhanced, and the attainment of the "neutral point" is rendered much easier by having the solution well acid with sulphuric acid.

Care should be taken that the ferricyanide spot

indicator is freshly prepared, and that it is quite free from ferrocyanides; the crystals of ferricyanide should be rough washed before dissolving them.

ESTIMATION OF VANADIUM IN STEEL.

COLORIMETRIC METHOD.

This method will be found to be of particular use where large numbers of steel assays have to be run through regularly. It depends upon a well known chemical reaction, and calls for the employment of Stead's chromometer with tubes graduated to 100 c.c. capacity.

A standard steel of known vanadium content, and somewhat similar to the sample worked upon, should be used; or a standard can be made by dissolving a plain steel containing no vanadium, adding to the solution known amounts of vanadium in standard vanadium solution, of chromium in the form of standard dichromate solution, or of nickel in the form of standard nickel-ammonium-sulphate solution.

Details of the Process.—Weigh off 1 gramme of the standard and of each of the samples. Transfer each weighed portion to a 12.2×9.7 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Jena or Bohemian beaker with a distinctive mark on each.

Add 50 c.c. of 20 per cent. nitric acid.

Boil till dissolved.

Cool the solutions.

Add 2 grammes of sodium bismuthate to each, and stir briskly.

Filter, collecting the filtrate (and washings) from the sample to be tested in the glass cylinder of the chromometer.

Wash twice with cold water.

Cautionously add solution of sulphurous anhydride till the liquid is decolourised.

Add 30 c.c. of 3 per cent. hydrogen peroxide solution.

Make up with water to 75 c.c.

Treat the filtrate (and washings) from the standard in the same way, and proceed to compare in the chromometer.

The percentage of vanadium is deduced by inverse proportion from the respective lengths of the columns of standard and sample.

Hydrogen peroxide imparts a mahogany colour to solutions containing vanadium, which deepens on standing—the standard and samples, however, should be “peroxidised” at the same time, and it is a matter of no moment whether the colour is “developed” in the beaker or the chromometer tube.

Titanium would interfere with the estimation.

ESTIMATION OF MOLYBDENUM.

ESTIMATION OF MOLYBDENUM IN STEEL.

Outline of the Process.—A weighed portion of the sample is treated with acids so as to dissolve the sample and cause the formation of insoluble tungstic oxide, which is separated on a filter from the other constituents. Sodium hydrate solution is added to the filtrate in quantity sufficient to neutralise the free acid but not to cause precipitation. The filtrate is then run cautiously into excess of hot sodium hydrate solution. By this means molybdenum is held in solution while the other constituents, except a little chromium, are precipitated. The precipitate is collected and washed. Lead acetate and ammonium acetate solutions are added to the filtrate and washings in order to precipitate the molybdenum as lead molybdate. This is filtered off, washed, dried, ignited, and weighed.

Details of the Process.—Weigh off 2 grammes of the sample, which should be in the form of fine drillings or turnings.

Transfer the weighed portion to a 600 c.c. Bohemian or Jena beaker.

Add 50 c.c. of 1.16 specific gravity hydrochloric acid.

Cover the beaker with a clock glass and heat nearly to the boiling point.

Add, a few drops at a time, 1.42 specific gravity

nitric acid. This causes a frothing, which should be allowed to subside before adding more. By the use of such a large excess of hydrochloric acid (which, although hot, is kept as concentrated as possible) the steel may be decomposed by adding very little more nitric acid than is necessary to oxidise the iron, without causing (and this is important) any separation of tungstic oxide. When complete decomposition has been effected, the iron should be in the ferric condition, and a black film of carbonaceous matter will have separated.

The solution, which has been maintained below boiling point, should now be boiled.

Evaporate as rapidly as possible to very low bulk, but not beyond pastiness.

Add a mixture of 40 c.c. of hot water, and 15 c.c. of 1.16 specific gravity hydrochloric acid.

Boil for two or three minutes.

Pour the solution, now containing a precipitate of tungstic oxide, into a 12.5 cm. Swedish filter. Wash well with water slightly acidulated with hydrochloric acid, collecting the filtrate and washings in a 300 c.c. conical flask.

The washed precipitate, if not too cumbersome, may be weighed, &c., for the estimation of tungsten (see p. 283 for notes on precautions).

To the filtrate add solution of sodium hydrate, shaking the flask well during and between each addition, until the free hydrochloric acid is neutralised. This occurs before the formation of a permanent precipitate, or even of a pronounced darkening of colour. It is important, in order to avoid a partial

precipitation of the molybdenum as basic ferric molybdate, to stop the neutralisation with caustic alkali before the darkening in colour takes place.

Transfer the solution (which with the washings should not exceed 350 c.c.) to a separating funnel.

Dissolve not less than 7 grammes of sodium hydrate in 150 c.c. of water in a 500 c.c. graduated flask, and heat the solution nearly to boiling point.

Run the solution in the separating funnel in a stream of rapid drops into the hot solution in the graduated flask, shaking the flask vigorously all the time.

By thus adding the partially neutralised mixture to the excess of caustic alkali, instead of operating in the converse manner, the molybdenum is held in solution as sodium molybdate. The iron and nearly all the chromium are precipitated as hydrates, but a small amount of the latter metal invariably passes into solution as sodium chromate.

Prepare a 28 cm. (about 11-inch) folded filter of No. 598 C. S. & S. or other thick filter-paper, set it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place in a large filter stand (see Fig. 7, p. 36). Allow the superfluous water to drain off.

Fill up the 500 c.c. flask to the containing mark with warm water. Close it with the stopper and mix the contents well.

Place a 250 c.c. graduated flask under the funnel.

Pour from the 500 c.c. flask into the filter, and

collect 250 c.c. of the clear filtrate. This represents 1 gramme of the sample.

Transfer the measured quantity to a 500 c.c. beaker.

Acidify with hydrochloric acid, using methyl orange as an indicator.

Add 5 c.c. more of 1.16 specific gravity hydrochloric acid. This excess is added to correct a tendency to the contamination of the lead molybdate (to be subsequently precipitated) with basic compounds.

Add sulphurous acid (see p. 172) to reduce the small amount of sodium chromate which is usually present.

Boil.

Add 40 c.c. of ammonium acetate solution (see p. 401). This not only substitutes free acetic acid, in which lead molybdate is insoluble, for the free hydrochloric acid, but serves to prevent the precipitation of lead sulphate.

Add 6 c.c. of lead acetate solution (see p. 341).

Collect the precipitate of lead molybdate in a 12.5 cm. Swedish filter.

Wash with hot water.

Place the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), cover with paper and allow to dry on a hot plate.

Ignite in a tared porcelain capsule. Prolonged ignition at a high temperature is not harmful.

Allow to cool in a desiccator.

Weigh and note the weight.

EXAMPLE—

	Grammes.
Weight of crucible + ash + precipitate	= 17·0362
„ crucible	= 16·9123
„ ash + precipitate	= 0·1239
„ ash	= 0·0008
„ precipitate	= 0·1231

The pure cream-coloured, ignited precipitate of PbMoO_4 , contains 26·15 per cent. of molybdenum, and when half of the solution from 2 grammes has been precipitated, washed, dried and ignited, the factor for calculating the percentage is 26·15.

$$\text{Log } 26\cdot15 = 1\cdot4174717.$$

$0\cdot1231 \times 26\cdot15 = 3\cdot219$ = percentage of molybdenum in the sample of steel.

NOTES.*—The estimation of molybdenum in steel as carried out by this process is not interfered with by any of the usual elements found in steel, such elements being either precipitated along with the iron or exerting no influence in the subsequent precipitation of the molybdate with lead acetate: this remark, of course, does not apply to tungsten.

* Ibbotson and Brearley, *Chemical News*, 8th June, 1900.

Results of Experiments Instituted by Ibbotson and Brearley to determine whether molybdenum in steel interferes with the estimation of the other elements, and how its interference may be overcome :—

Silicon.—Molybdenum does not interfere.

Manganese.—If estimated by separation of the iron with ammonium acetate and precipitation with bromine and ammonia, molybdenum exerts no influence. Unless a large excess of acetate is used, nearly all the molybdenum is precipitated with the iron.

Sulphur.—The gravimetric estimation of sulphur is accurate if the barium chloride is added to a distinctly acid solution in order to eliminate the possibility of contamination with BaMoO_4 , or basic ferric molybdates. The evolution method—*i.e.*, the dissolution of the steel in hydrochloric acid, the evolved sulphuretted hydrogen being passed through metallic solutions—is also uninfluenced by the presence of molybdenum. One would expect low results due to the formation of MoS_2 . This does not seem to be the case when strong hydrochloric acid is used to effect decomposition.

Phosphorus.—The rapid method, in which the phosphorus is precipitated in the presence of all the iron, gives high results, apparently in consequence of contamination of the yellow precipitate with

MoO₃. The difficulty may obviously be overcome by dissolving out in ammonia and precipitating with magnesia mixture.

Carbon.—The carbonaceous residue, after decomposing the sample with copper solutions, gives blue washings (Mo₃O₈) long after the copper salts have been washed out. The results, compared with direct combustions with PbO₂ or Pb₃O₄, are a few hundredths per cent. too low.

Iron.—On precipitating with ammonia, part of the molybdenum accompanies the iron; gravimetric results are, therefore, too high. The iron cannot be estimated by simply dissolving the sample and titrating, because the molybdenum, reduced by the liberated hydrogen to Mo₂O₃, falsifies the result by being oxidised to MoO₃. For a like reason ferric solutions containing molybdenum should not be reduced with zinc or stannous chloride. They may, however, be reduced with sulphurous anhydride, and titrated accurately either with bichromate or permanganate. Potassium ferro-cyanide does not certainly indicate ferric iron, on account of the very ready formation of a deep brown precipitate with MoO₃ solutions.

ESTIMATION OF MOLYBDENUM IN CAST IRON.

Proceed as directed for steel in the foregoing pages.

Where tungsten in considerable amount was present, Brearley and Ibbotson found it advantageous to filter off the graphite, burn the filter at low redness, and fuse the residue with potassium nitrate.

**ESTIMATION OF MOLYBDENUM IN FERRO-MOLYBDENUM
AND FUSED MOLYBDENUM.**

These alloys are readily attacked by acids, and molybdenum may be estimated as directed in the foregoing pages.

THE ESTIMATION OF VANADIUM, MOLYBDENUM,
CHROMIUM, AND NICKEL IN STEEL.

The method here detailed gives the result of successful investigation and discovery by Mr. ANDREW A. BLAIR, and is taken, by permission, from the *Journal of the American Chemical Society*, August, 1908.

Details of the Process.—Dissolve 2 grammes of the sample in nitric acid with the addition of hydrochloric acid if necessary, evaporate to dryness, re-dissolve in hydrochloric acid, and evaporate until the solution is syrupy. Dissolve in a small amount of hydrochloric acid of 1.1 specific gravity, cool in ice cold water, and wash into a separatory funnel of about 250 c.c. capacity with as small an amount as possible of acid of the same strength. The separatory funnel should be conical in shape, and should be fitted at the lower end with a Geissler stop-cock, and at the upper end with a glass stopper. Both stopper and stop-cock should be most carefully ground to prevent leakage. Add to the solution in the funnel about 80 c.c. of ordinary ether, and shake vigorously for half a minute. An ordinary clamp with cork-lined jaws, supported on a stand, makes a convenient arrangement for holding the funnel. When the two strata have separated, open the stop-cock and allow the lower to run into another separatory funnel. Remove the stopper, wash the solution down with about 10 or 15 c.c. of hydrochloric acid of 1.1 specific gravity, shake again, and allow the washings to run

into the other funnel. Add 50 c.c. of ether to the solution in the second funnel to remove as much of the remaining iron as possible, run the acid solution into a beaker, and evaporate nearly to dryness. Add nitric acid in excess, and evaporate until all the hydrochloric acid is expelled, and finally, when the solution is almost syrupy, add 20 c.c. of hot water. Heat the solution, and add a few drops of sulphurous acid to reduce any chromic acid that may have been formed. Boil and pour the solution slowly, stirring vigorously, into a boiling solution of sodium hydroxide containing 100 grammes sodium hydroxide to the litre. Boil the solution for a few minutes, allow the precipitate to settle, filter, wash twice by decantation and finally on the filter until the filtrate measures about 300 c.c. in volume. The precipitate consists of the oxides of chromium, nickel, and iron, with the greater part of the manganese and any copper that may have been in the sample. The filtrate contains the vanadium, some silica and alumina from the sodium hydroxide, and sometimes a little chromium. Add dilute nitric acid to the filtrate until it just turns blue litmus paper red, then add a few drops of sodium hydroxide solution to make it alkaline, boil and filter. To the filtrate add 10 c.c. of a 10 per cent. solution of lead nitrate, and then enough acetic acid to make it decidedly acid, and boil for several minutes. Filter the precipitate which contains all the vanadium as lead vanadate, and wash with hot water. Dissolve in hot dilute hydrochloric acid, evaporate nearly to dryness, add 50 c.c. of hydrochloric acid, and evaporate again, add 10 c.c. of strong sulphuric acid, and evaporate until it fumes freely.

Allow it to cool, and when cold dilute to 150 c.c., heat to a temperature of 60° or 70°, and titrate with permanganate. The iron value of the permanganate solution multiplied by 0.9157 gives the vanadium. The method of reducing vanadium by evaporating with hydrochloric acid, and then driving off the hydrochloric acid as proposed by Campagne (*Compt. Rend.*, 137, 570, 1903), gives most excellent results. The presence of small amounts of iron does not affect its accuracy, and the trouble of boiling off every trace of sulphurous acid when this reagent is used is avoided.

The two precipitates obtained from the sodium hydroxide solution contain chromium, nickel and copper, besides iron and manganese. Ignite the two filters and precipitates, and fuse with about 2 grammes of sodium carbonate and half a gramme of potassium nitrate. Treat the fused mass with water and filter. The insoluble portion contains the nickel, copper, iron, and part of the manganese, and the filtrate the chromium and the rest of the manganese. To the filtrate add ammonium nitrate in sufficient quantity to change all the sodium salts to nitrates, and evaporate to a small bulk, adding a few drops of ammonia from time to time. Dilute to about 50 c.c., boil, filter, and wash with hot water. The insoluble matter consists of manganese and any silica, alumina, &c., that may have been in the reagents. Boil the filtrate to drive off the ammonia, add sulphurous acid to reduce the chromic acid, boil off the excess and precipitate by ammonia. Filter, wash, ignite, and weigh the chromium sesquioxide which contains 68.46 per cent. of chromium.

Return the filter, containing the insoluble matter from the fusion, to the crucible in which the fusion was made, ignite, dissolve in hydrochloric acid, dilute, precipitate the copper by hydrogen sulphide, filter, and evaporate the filtrate with excess of sulphuric acid until the hydrochloric acid is expelled. Dilute, add excess of ammonia, and precipitate the nickel by electrolysis. A current of about $4\frac{1}{2}$ amperes is sufficient, and the iron and manganese present do not interfere with the accuracy of the results.

To the ethereal solution of the iron, which remains in the two separatory funnels, add water and shake. Draw off the ferric chloride containing the molybdenum, which separates from the ether, and evaporate nearly to dryness, add 10 c.c. strong sulphuric acid, and evaporate carefully until the hydrochloric acid is driven off, and the sulphuric acid fumes freely. Cool, dissolve in about 100 c.c. of water, and carefully deoxidize with ammonium bisulphite, boil off the excess of sulphurous acid, and cool the solution. Transfer the cold solution to a pressure bottle of 200 c.c. capacity and pass a current of hydrogen sulphide through it until it is saturated, close the bottle and heat it on a water bath for several hours. Allow it to cool slowly. Filter on a Gooch crucible, wash the precipitate first with water containing a little sulphuric acid, and finally with alcohol. Place the Gooch crucible containing the precipitate on a small triangle placed inside a large porcelain crucible, so that the bottom of the Gooch crucible shall not touch the bottom of the porcelain crucible. Cover the latter with a watch-glass and heat it carefully, raising the heat gradually until

there is no smell of sulphurous acid. Replace the watch-glass with a porcelain cover, and heat until the precipitate of molybdenum sulphide becomes bluish-white in colour.

Place the Gooch crucible over a lamp and heat it to faint redness, cool and weigh. Heat it again to faint redness, weigh, and repeat the operation until it ceases to lose weight. Place the crucible on the vacuum flask, and dissolve the molybdic trioxide in dilute ammonia, wash, heat, and weigh the crucible. The difference between the two weights is molybdenum trioxide, which contains 66.67 per cent of molybdenum. There always remains on the felt of the Gooch crucible a small amount of ferric oxide.

Mr. Blair found it necessary to precipitate the molybdenum sulphide from a sulphuric acid solution, as it seemed almost impossible to separate all the molybdenum sulphide in one operation from a hydrochloric acid solution. Figures are given to show the remarkable accuracy of the method.

ANALYSIS OF QUICK-CUTTING TOOL STEEL.

PREPARATION OF THE SAMPLE.

Quick-cutting, self-hardening, or high-speed steel is, in its finished state, too hard to be drilled or turned. It must, therefore, be softened. This is conveniently done in works by embedding the sample in lime, sand, or fine ashes contained in a cast-iron or malleable-iron tube or box, ramming up tightly, placing in a smith's hearth, slowly raising the temperature, and keeping the whole till the sample has been "soaked" at a red heat for an hour or two. The sample may be allowed to cool gradually in the hearth, or may be left for some hours under hot ashes.

According to Ibbotson, the sample can be effectually softened without suffering decarbonisation by putting it in a muffle furnace, surrounded on all sides by lime or bone ash rammed tightly. The muffle is brought to a full red heat, and, after being maintained in this condition long enough for efficient "soaking," is allowed to cool slowly. When the temperature has fallen low enough to permit the insertion of the hand without discomfort, the steel may be withdrawn and can then be drilled with ease.

By the use of suitable tools, and by careful, intelligent working, fine drillings or turnings may be obtained.

Drillings or turnings from the skin of the sample should, of course, be rejected.

When drilling cannot conveniently be done, the steel may be broken into small pieces for analysis.

ESTIMATION OF CARBON.

Weigh off 4 grammes of the sample, which should be in the form of fine turnings or drillings, and estimate by direct combustion *at a bright red heat*. Full details are given on pp. 98 to 111.

ESTIMATION OF CHROMIUM.

GALBRAITH'S METHOD MODIFIED.*

Weigh off 2.4 grammes of the sample, which should be in the form of fine turnings or drillings.

Transfer the weighed sample to a 300 c.c. conical flask.

Add a mixture of 20 c.c. of concentrated sulphuric acid and 100 c.c. of water.

Heat gently, and when most of the drillings are broken up, boil rapidly down to small bulk—until solid ferrous sulphate begins to separate, or until the liquid bumps dangerously. A copious black residue remains.

Cautiously add 200 c.c. of warm water, and heat the liquid to the boiling point.

Add crystals of potassium permanganate, in very small quantities at a time, till the oxidation of the

* From an account by Ibbotson in *Technics*.

iron to ferric sulphate, and chromium to chromic acid has been effected. This point is indicated when a brown precipitate is formed, which persists after boiling for a few minutes. Tungstic oxide may separate out at this period.

Add more (but not more than $\frac{1}{2}$ gramme) crystals of potassium permanganate.

Wash down any small crystals adhering to the sides of the flask.

Boil vigorously for three minutes, taking care to avoid bumping.

Transfer to a 300 c.c. graduated flask.

Cool.

Dilute to the mark, with an extra allowance of 1 c.c. for the volume of the manganese peroxide precipitate.

Filter through two dry filters into a 250 c.c. graduated flask till the filtrate reaches the mark.

The chromium and iron should now be in their highest state of oxidation.

Pour the measured portion of the filtrate into a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Wash out the 250 c.c. graduated flask, collecting the washings in the same basin.

Add about 20 c.c. of sulphuric acid.

Get ready the articles noted on p. 214, as required for titration.

Proceed with the titration as directed on pp. 214-216.

ESTIMATION OF TUNGSTEN.

The estimation may be made as directed on pp. 281 to 287.

ESTIMATION OF MOLYBDENUM.

The estimation may be made as directed on pp. 290 to 294.

ESTIMATION OF MANGANESE, PHOSPHORUS,
AND SULPHUR.

“The decomposition of a high-speed steel with aqua regia is readily accomplished, and, after the removal of tungsten and silicon, the filtrate readily lends itself to the determination of sulphur, phosphorus and manganese.”—Ibbotson in *Technics*.

In the solutions from weighed quantities of the sample proceed to estimate these constituents as in ordinary steel.

ANALYSIS OF ALLOYS USED IN THE MANUFACTURE OF QUICK-CUTTING STEEL.

PREPARATION OF THE SAMPLE.

Many of the alloys used in the manufacture of quick-cutting, high-speed, or self-hardening steels may be made fit for turning or drilling by the heat treatment previously described (see p. 303).

Some of the alloys may be crushed and reduced to powder in a hardened steel mortar, and the pulverising finished, where necessary, in an agate mortar. For carbon estimations the powder will be fine enough if it can readily pass through a 60-mesh sieve.

ESTIMATION OF CARBON.

One or two grammes of the sample, according to the presumed percentage of carbon, in the form of fine turnings or of powder which has readily passed through a 60-mesh sieve, are intimately mixed with 6 grammes of copper oxide and 2 grammes of litharge, placed in a magnesite boat, or a fireclay boat with a lining of asbestos paper, and combustion proceeded with as described on pp. 186 to 199.

The aspiration of air or oxygen should be carefully controlled, and the temperature should be gradually raised to redness so as to avoid too rapid an evolution

of carbon dioxide. In the case of ferro-chrome, for instance, the purified air current should be aspirated for an hour after the highest possible temperature of the furnace has been reached. When the boat is removed after the combustion, the contents, with the exception of a few beads of metallic lead, should be black in colour and should show signs of complete fusion.

ESTIMATION OF TUNGSTEN.

The following excellent method was published by Ibbotson in *Technics* :—

“Many ferro-tungstens can be decomposed by treating them with a large excess of warm, but not boiling, hydrochloric acid, and then adding concentrated nitric acid a few drops at a time. Highly chromiferous alloys are much too refractory, however, and the following method, which is equally suitable for those which are free from chromium, gives very good results with alloys of all degrees of richness. One gramme of the alloy, through a 60-mesh sieve, is placed in a deep and capacious platinum dish provided with a lid. From 10 to 15 c.c. of hydrofluoric acid solution are then added, and the action accelerated by gently warming for no more than two minutes. The lid of the dish is then pushed aside slightly, and concentrated nitric acid added three or four drops at a time. After each addition a very vigorous action sets in, accompanied by much frothing and a copious

evolution of nitrous fumes, thus making it necessary to push the lid smartly back into position and to wait for at least a minute between each addition of the nitric acid. When the addition of the nitric acid causes no further audible action (a condition which is frequently reached after the operation of adding the three or four drops has been repeated the same number of times), the alloy has gone completely into solution with the exception of a small carbonaceous residue. The dark green solution is then allowed to digest for five minutes, and then 5 to 10 c.c. of concentrated sulphuric acid are cautiously added in drops, the lid being pushed aside slightly for the purpose.

"It is now permissible to evaporate the solution until thick fumes of sulphur trioxide escape, when the whole of the tungstic oxide will have separated. During the earlier stages of the evaporation there is a marked tendency to frothing, due apparently to the decomposition of the carbonaceous residue left unattacked by the mixture of hydrofluoric and nitric acids. It is therefore advisable to exercise considerable vigilance until this stage has been passed. The subsequent evaporation may be hastened by heating over a rose burner, but the lid of the dish should not be removed during the process.

"When copious fumes of sulphur trioxide escape, the evaporation is stopped, and, after cooling the dish, 10 c.c. of hydrochloric acid are very cautiously added, and then an equal quantity of water. The mixture is warmed for a few minutes, and the whole mass then transferred by means of the wash bottle to a capacious beaker. Except for an obstinate iridescent film on

the sides and bottom of the dish, the 'policeman' effectually removes the whole of the insoluble residue.

"The bulk of the liquid in the beaker is made up, if necessary, to about 100 c.c. with distilled water, the whole brought to boiling, and maintained in ebullition for five minutes.

"In the meantime a pulp filter (see p. 154) should be prepared, on which the tungstic oxide is collected after allowing a short time for settling. The precipitate is washed with hot water slightly acidulated with hydrochloric acid, and then transferred to the ignition dish or crucible.

"A tiny piece of ashless filter-paper soaked with one drop of ammonium hydrate will remove the film of tungstic oxide referred to above, and this can be ignited with the main precipitate.

"After ignition, the mass of tungstic oxide is invariably discoloured by contamination with ferric and chromic oxides. The amounts of these depend on many circumstances, such as, for instance, the richness of the alloy and the rate at which the preliminary 'opening out' and subsequent evaporation have been conducted. Amounts varying from 1 centigramme of ferric oxide associated with 2 milligrammes of chromic oxide, to as much as eight times each of these quantities, have been found.

"The ferric and chromic oxides are determined precisely as described under the determination of tungsten in steel" (see p. 281).

ESTIMATION OF CHROMIUM.

Proceed as directed on pp. 207 to 211.

ESTIMATION OF SULPHUR, PHOSPHORUS,
AND MANGANESE.

The following method of "opening out," details by Horace Jervis (*Chemical News*, 5th December, 1902) and F. Ibbotson, will be found serviceable:—

To every 2.5 grammes of the sample, which should be in very fine powder or in fine drillings in a tall beaker, add 20 c.c. of 1.42 specific gravity nitric acid, and then, in small quantities at a time, add about 25 c.c. of 1.16 specific gravity hydrochloric acid.

When the action subsides, add a few crystals of potassium nitrate and apply a gentle heat with a clock glass cover in position. The mixture must not be heated to the boiling point, as this would cause bumping and would weaken the acids.

Continue to digest at a temperature near to but under the boiling point for twenty-four hours or so. A yellow residue of tungstic oxide will form (if tungsten was present). A green colour indicates imperfect decomposition.

When decomposition is complete, evaporate the liquid to low bulk, dilute with water, and separate the residue by filtering and washing. The filtrate and washings may be collected in a graduated flask, cooled, made up to the mark with water, and mixed thoroughly. Measured quantities may be withdrawn and used for the estimation of sulphur, phosphorus and manganese by the usual gravimetric methods.

MISCELLANEOUS ESTIMATIONS.

ESTIMATION OF MANGANESE IN FERRO-MANGANESE, SPIEGEL-EISEN, SILICO-SPIEGEL, &c.

GRAVIMETRIC METHOD.

Outline of the Process.—The weighed sample is dissolved and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a precipitate consisting of basic hydrate and acetate of iron is formed, while the manganese remains in solution. These are separated by filtering and washing. To save the full amount of washing required to remove all the manganese from the precipitate it is found convenient to wash the precipitate once, dissolve and re-precipitate the iron, and again wash. Bromine is added to the mixed filtrates and washings, and, on adding ammonia, hydrated manganese oxide is precipitated. This is collected, washed, and ignited. The percentage of manganese is ascertained from the weight of the finished residue of Mn_2O_4 .

Details of the Process.—Weigh off 0.5 gramme of the sample. Transfer the weighed portion to a 1.200 c.c. (about 40-oz.) globular Bohemian flask.

Add 5 c.c. of 1.42 specific gravity nitric acid, 5 c.c. of 1.16 specific gravity hydrochloric acid, and 5 c.c. of water.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 20 c.c. of hot water.

Boil.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after violent shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 400 c.c. of cold water.

Add 15 c.c. of ammonium acetate solution (see p. 162).

Boil briskly over the flame of a 16 mm. (about $\frac{5}{8}$ -inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is dangerous.

Prepare a 24 cm. (about 9 $\frac{1}{2}$ -inch) fluted filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large filter stand—see Fig. 7, p. 36. Set under it a 1,200 c.c. (about 40-oz.) Phillips' conical beaker on a dry cork mat.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove

the flask till the brisk action ceases; replace on the tripod, and allow the rapid boiling to continue. It may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear yellowish-coloured liquid should drain away quickly when on the filter. The yellow colour of the liquid is due to dissolved carbide.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask with hot water and pour the rinsings on to the filter, and allow the liquid to drain off thoroughly into the conical beaker. Keep the globular flask, without more washing, for further use.

Wash once with hot water, collecting the washings in the conical beaker.

Take away the conical beaker and reduce the bulk of the liquid by boiling.

Place the 40-oz. globular Bohemian flask under the stem of the funnel.

From a wash bottle direct a stream of acidulated water (1 of 1.16 specific gravity hydrochloric acid to 2 of water) on to the precipitate so as to dissolve it.

When all the precipitate has dissolved, take away the globular flask and boil the solution.

Neutralise by adding ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after vigorous shaking.

Make up to about 400 c.c. with cold water.

Add 15 c.c. of ammonium acetate solution (see p. 162).

Boil briskly, as before.

Prepare a 24 cm. folded filter of thick paper, as before, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, place it in the large stand with a 600 c.c. beaker under the stem of the funnel.

Allow the *boiling* to continue for about half a minute, avoiding loss by frothing.

Immediately the boiling has finished, pour the contents of the flask into the prepared filter.

Rinse the flask twice with hot water and pour the rinsings into the filter, and allow the liquid to drain off thoroughly into the beaker.

Wash three times with hot water, collecting the washings in the beaker.

Cautiously pour the liquid from the beaker into the conical beaker containing the first filtrate, (It is advisable to collect the second filtrate in a vessel apart from the first filtrate.)

Cool the filtrate and washings.

Add about 8 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is nearly all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about fifteen minutes after brominating.

Cautiously add enough ammonia liquor to make the solution faintly alkaline.

Stir cautiously at first, and allow to stand for a few minutes.

Boil till some of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off most of the excess ammonia.

Filter through two 12.5 cm. Swedish filter-papers, and wash each four or five times with hot water.

Place the funnels containing the filter-papers and precipitates on dryers on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried papers and precipitates in a tared platinum or porcelain crucible in a muffle furnace which is at a red heat. Allow to remain in a very hot muffle for thirty minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Make the necessary correction for co-precipitated iron (see p. 38), and calculate the percentage of manganese from the weight of Mn_2O_4 (which contains 72.052 per cent. of manganese) obtained from the half gramme of sample.

ESTIMATION OF SILICON IN FERRO-SILICON, &c.

Ferro-silicon containing less than 18 per cent. of silicon may be decomposed by acids; those containing more silicon require different treatment. For the lower grade materials—those made in blast-furnaces as distinguished from the products of the electric furnace—the following method gives satisfactory results:—

Weigh off about 0.8 gramme of the sample, which has been pulverised to a very fine powder in an agate mortar.

Transfer the weighed portion to a Berlin basin of about 11 cm. (about $4\frac{1}{2}$ inches) diameter.

Add about 5 c.c. of water and boil gently.

Stir well with a glass rod.

Raise the rod about 2.5 cm. (about 1 inch) and pour down it about 30 c.c. of 1.16 specific gravity hydrochloric acid and 15 c.c. of 1.42 specific gravity nitric acid.

The addition of a strong solution of ferric chloride with some tartaric acid facilitates solution.

Cover the basin with a clock glass and boil briskly for fifteen minutes.

Dilute with about 30 c.c. of hot water and mix well by stirring.

Pour into a 12.5 cm. Swedish filter.

Wash with acidulated water (water, 4 parts; 1.16 specific gravity hydrochloric acid, 1 part) several times, then two or three times with water.

Dry the residue by placing the funnel paper and contents on a filter dryer (Fig. covering with paper, and allowing to dry on hot plate.

Place the dried residue and filter-paper in a platinum or porcelain crucible or capsule.

In a hot muffle furnace burn off the filter and ignite for about half an hour.

Withdraw the crucible or capsule and cool, allow to cool in a desiccator.

Weigh quickly and note the weight.

By the foregoing procedure a result satisfactory for general works' purposes may be obtained. But if a more exact estimation is required, the residue may be subjected to purification, as on p. 16, and the first filtrate may be treated in the following manner:—

Evaporate to dryness, and, when the beaker is cool enough, add 30 c.c. of 1.16 specific gravity concentrated hydrochloric acid, and evaporate. When the beaker is again cooled sufficiently, add 20 c.c. of hydrochloric acid and 10 c.c. of water and boil briskly, then filter through a 9 cm. Swedish filter, wash the small residue with acid and water, dry, ignite, and weigh. The weight of the residue should then be added to the weight of the purified residue and the percentage calculated on the quantity of sample taken. For exact calculation see p. 17.

For the decomposition of higher-grade ferro-alloys—those prepared in electric furnaces—fusion

very finely-pounded sample in fusion mixture gives good results. 0.5 of the sample may be fused with 8 grammes of the fusion mixture (see p. 346), the melt extracted and dissolved in the usual manner (except that, as a nickel capsule has been used, no acid should be used in loosening the melt from it), made up to 1 litre, and one-fourth withdrawn, evaporated, and finished.

Sodium peroxide may be used to decompose high-grade ferro-silicon, taking about 7 grammes for 0.5 gramme of the finely-powdered sample of 50 per cent. ferro-silicons and 8 grammes or more of peroxide for richer samples. Mix these in a nickel capsule, heat cautiously till fusion begins, raise the temperature to dull redness, and complete the fusion. Allow to cool, dissolve, and wash out with water and acidify. Evaporate to dryness, take up with acid, filter, and wash. As a precaution, evaporate the filtrate and washings, and recover any silica present. Weigh, and note the weight. After weighing, the silica may be volatilised by hydrofluoric and sulphuric acids.

0.5 gramme of finely-powdered sample may be mixed with 10 grammes of fusion mixture (see p. 346), and 2.5 grammes of powdered potassium nitrate, cautiously fused, and treated as above.

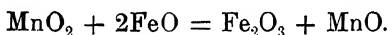
Stead's tribasic reagent (see p. 346) may be used to decompose rich ferro-silicons, and potassium bisulphate has also been recommended.

VOLUMETRIC ESTIMATION OF MANGANESE.**BASED ON PATTINSON'S METHOD.****ESTIMATION OF MANGANESE IN ORE.**

Outline of the Process.—A weighed quantity of the finely-pounded sample is dissolved in acid, or, if necessary, is fused, and the melt is dissolved. By the action of bleaching powder the iron in the ore is converted into the ferric state, and the manganese is also converted to one of its highest states of combination.

A known amount (which must be in excess) of ferrous salt or solution is then added. Some of this is converted into the ferric condition by the action of the manganese compound in the solution.

For convenience, the reaction may be represented thus :—



The excess of ferrous oxide is ascertained by titrating with standard dichrome solution, and from the difference (that is, the amount oxidised by the manganese salt), the percentage of manganese in the ore is ascertained.

Details of the Process.—Weigh off 0.5 gramme of the finely-pounded sample.

Transfer the weighed portion to a 12.5×10 cm. (about 5×4 inches) beaker.

Add 10 c.c. of 1.16 specific gravity hydrochloric acid.

Boil till all the manganese oxide is dissolved, and much of the excess acid has been driven off.

If the ore is not readily soluble in acid, decompose by fusion in the following manner:—

Weigh off 6 grammes of fusion mixture (see p. 346).

Spread the weighed portion in a 7.5 cm. (about 3 inches) diameter nickel or platinum capsule.

Weigh off 0.5 gramme of the finely-pounded sample of ore.

Mix the ore carefully with the fusion mixture
Fuse over a blowpipe or in a muffle furnace.

When cool, place the capsule in a glazed porcelain basin of 18 cm. (about 7 inches) diameter.

Pour water into the capsule and allow the melt to loosen or dissolve.

Pour the solution into a 12.5 × 10 cm. (about 5 × 4 inches) beaker.

Rinse the solution in the porcelain basin into the beaker.

Rinse the remainder of the melt from the capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the capsule any still-clinging melt may be loosened.

Add hydrochloric acid to the liquid in the beaker—more than enough to neutralise, and to dissolve the soluble matter.

Almost cover the beaker with a clock-glass.

Evaporate on a hot plate to small bulk, and to remove excess of acid.

Rinse the cover and the inside of the beaker with warm water.

By whichever method the sample has been attacked :—

Add to the solution in the beaker solid pure precipitated calcium carbonate until a slight permanent precipitate forms.

Redissolve the precipitate by adding a small quantity of hydrochloric acid—leaving the solution faintly acid.

Add 5 c.c. of 10 per cent. zinc chloride solution (see p. 173).

Add about 300 c.c. of boiling water, and about 70 c.c. of bleaching powder solution (see p. 339) to which just enough hydrochloric acid has been added to give it a faint permanent greenish-yellow colour after gentle agitation. The object of this addition of acid is to prevent a local precipitation of manganese in a lower state of oxidation than MnO_2 . The solution should remain clear on the addition of the bleaching powder.

Stir the liquid, and gradually add about 5 grammes of pure calcium carbonate diffused in about 25 c.c. of hot water. After the first evolution of carbonic acid (during which time the cover is kept on the beaker) has ceased, the precipitate is stirred to make it collect together, about 2 c.c. of methylated spirits are added, and it is again stirred. This should cause the formation of a quickly-settling precipitate containing all the manganese as dioxide.

Collect the precipitate in an 18 cm. plaited filter, collect the filtrate (and washings) in a beaker of convenient size.

Wash several times with cold water, and, when the greater part of the chlorine has been removed, with warm water (about 70°C.). Continue the washing

until on testing with acidulated silver nitrate solution (see p. 170) no chlorine appears to be present. Wash three times more with warm water.

Place the precipitate and filter-paper in an 18 cm. (about 7 inches) diameter porcelain basin.

Measure about 20 c.c. of water and about 10 c.c. of 1.84 specific gravity sulphuric acid into the basin.

Stir, so as to mix the water and acid.

Weigh off, accurately, about 5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Titrate, as directed on pp. 130 to 133.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example:—

EXAMPLE—		Grammes.
Weight of ore taken	=	0.5026
„ of Mohr's salt taken	=	5.1324
Iron in Mohr's salt taken =	$\frac{5.1324 \times 14.26}{100}$	= 0.73188

Dichrome solution required = 23.2 c.c., of which each c.c. = 0.0102 gramme of iron.

$$23.2 \times 0.0102 = 0.23664.$$

Iron in Mohr's salt	=	0.73118
„ represented by the standard dichrome used	=	0.23664
„ oxidised by MnO_2 in the sample of ore	=	<u>0.49454</u>

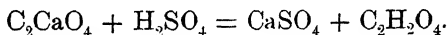
The equation formerly given shows that 111.8 parts, by weight of iron, are equivalent to 55 parts, by weight of manganese.

$$\frac{0.49454 \times 55 \times 100}{111.8 \times 0.5026} = \frac{0.49454}{0.5026} \times 49.19 = 48.40$$

= percentage of manganese in the sample of ore.

**RAPID ESTIMATION OF LIME IN LIMESTONE,
DOLOMITE, OR SLAG.****ULK'S (VOLUMETRIC) METHOD.**

Outline of the Process.—The weighed portion of the finely-pounded sample is treated with acid to dissolve the soluble constituents, and these are separated by filtration and washing. When experience of this rapid method has been gained, it may not be necessary to separate the insoluble matter. The filtrate and washings are neutralised, and hot ammonium oxalate solution is added to precipitate the lime. The precipitate is collected, washed, and dissolved in excess of sulphuric acid. By this means the calcium oxalate is decomposed, calcium sulphate and oxalic acid being formed—



The amount of oxalic acid present is measured by the reduction, and decolourising, of standard potassium permanganate solution.

A decinormal solution of potassium permanganate contains 3.163 grammes per litre, and 1 c.c. of such a solution corresponds to 0.0063 gramme of crystallised oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), or 0.0028 gramme of lime.

A solution containing 11.2967 grammes of pure potassium permanganate per litre corresponds to 0.01 gramme of lime per c.c.

A standard solution of this strength may be made as directed on p. 121, and standardised either with standard solution of oxalic acid, or with Mohr's salt as directed on pp. 123 and 125.

A permanganate solution which has been prepared for the estimation of iron and standardised may be used, the factor for Fe $\times 0.50089$ corresponding to CaO, or 0.01 gramme of Fe corresponding approximately to 0.005 gramme of lime when titrated with standard potassium permanganate solution. As 0.5 gramme of sample is usually taken for the estimation of CaO, the Fe factor will, of course, approximately correspond without correction.

In standardising with oxalic acid the directions given in *Sutton's Volumetric Analysis* should be followed.

The measured solution is "brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 58° C., and the permanganate measured from a burette. The colour disappears slowly at first but afterwards more rapidly, becoming at first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid, nevertheless, it is as reliable with care and attention."

Details of the Process.—Weigh off 0.5 gramme of the finely-pounded sample.

Transfer the weighed portion to a 500 c.c. beaker.

Add 6 c.c. of 1.42 specific gravity nitric acid along with 30 c.c. of hot water.

Boil till all the soluble constituents are dissolved.

Add about 150 c.c. of water and a drop or two of strong sulphuric acid.

Heat to boiling point and cautiously add ammonia liquor (stirring constantly during the addition) till the solution is just neutral.

Add 70 c.c. of hot ammonium oxalate solution (see p. 163). This will cause the precipitation of calcium oxalate (CaC_2O_4) with perhaps a little iron.

Cover the beaker with a clock-glass and allow boiling to continue for a few minutes.

Allow the residue and precipitate to settle.

Collect on a 12.5 c.m. Swedish filter, collecting the filtrate (and washings) in a convenient sized beaker.

Wash two or three times with hot water and once with ammonia liquor. Wash twice more with hot water.

Wash, with warm water, the residue and precipitate from the filter into an 18 c.m. (about 7 inches) diameter porcelain basin.

Stir so as to thoroughly mix and make a cream of the washed off residue and precipitate with the water.

Add about 100 c.c. of water.

Cautiously add, with constant stirring, 25 c.c. of 1.84 specific gravity sulphuric acid.

Instead of the 100 c.c. of water and 25 c.c. of acid, 125 c.c. of sulphuric acid for lime estimation (see p. 345) may be used.

Stir the whole so as to dissolve the calcium oxalate.

Titrate with standard potassium permanganate solution, keeping the solution at a temperature of about 60° C. while titrating.

Calculate the percentage.

EXAMPLE.—0.503 gramme of the sample taken for the estimation. This required 26.83 c.c. of standardised potassium permanganate solution, each c.c. of which was equal to 0.0099 gramme of lime.

$$\frac{26.83 \times 0.0099 \times 100}{0.503} = 52.805 = \text{percentage of lime in the sample.}$$

ESTIMATION OF TITANIUM IN IRON ORES.

Weigh off 1 or 2 grammes of the finely-pounded sample.

Transfer the weighed portion, along with 1 gramme of sodium ammonium phosphate, to a 15 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 30 c.c. of 1.16 specific gravity hydrochloric acid.

Evaporate to dryness.

Weigh the residue and grind it in an agate mortar with 10 times its weight of sodium carbonate or fusion mixture.

Transfer to a nickel basin and fuse over a blow-pipe or a Mecker burner.

Allow to cool.

Boil with distilled water.

Collect the residue on a filter and wash.

With very little water wash the residue into a beaker.

Add 5 c.c. of 1.16 specific gravity hydrochloric acid, 2 c.c. of 1.51 specific gravity sulphuric acid, and 8 c.c. of water.

Evaporate until all the hydrochloric acid is expelled and white fumes of SO_3 come off.

Cool, dilute, boil, filter, and wash.

Dilute to about 150 c.c.

Add ammonia solution until a slight precipitate forms, just re-dissolve this in hydrochloric acid, and reduce with sulphurous anhydride solution.

As soon as the solution is colourless add 30 c.c. of 1.045 specific gravity acetic acid and 10 grammes of sodium acetate.

Boil.

Titanium oxide (TiO_2) will separate, but may be impure. If, however, it is re-dissolved and re-precipitated, the TiO_2 will be pure, and should be white.

Collect the precipitate on a 12.5 cm. Swedish filter and wash.

Dry the washed precipitate, ignite, allow to cool, weigh, and calculate the percentage.

The pure oxide contains 60.05 per cent. of titanium.

$$\text{Log } 60.05 = 1.7785130.$$

**ESTIMATION OF PHOSPHORUS IN PIG IRON
CONTAINING TITANIUM.**

Dissolve the weighed portion—say 2 grammes—in acid.

Evaporate to dryness, re-dissolve, filter, and wash.

Preserve the filtrate and washings.

Dry and ignite the residue, so as to drive off the graphite.

Fuse the ignited residue (which contains oxides of phosphorus, titanium, and iron) with sodium carbonate.

Extract the melt with hot water, filter, and wash.

Acidify the clear filtrate and washings with hydrochloric acid.

Add pure ferric chloride solution—more than sufficient to combine with the phosphoric anhydride present.

Cautiously add dilute ammonia liquor or solution of ammonium carbonate; ferric phosphate, which is white, will first be precipitated, and, on continuing to add ammonia solution or ammonium carbonate, the precipitate will become brown if enough ferric chloride is present.

Boil.

Collect the precipitate on a Swedish filter and wash with warm water.

Take away the beaker containing the filtrate and washings.

Place a clean beaker under the funnel and dissolve the precipitate on the filter by means of hydrochloric acid.

Wash the filter-paper with hot water, collecting the washings in the same beaker.

Evaporate the solution and washings to dryness, treat the dried residue with hydrochloric acid, and separate the insoluble residue on a filter.

Wash the residue, collecting the filtrate and washings in the beaker containing the first filtrate and washings.

Add 35 c.c. of ammonium nitrate solution and proceed with the estimation of phosphorus as directed on pp. 70 to 73.

VOLUMETRIC ESTIMATION OF SULPHUR IN SPECIAL STEELS.

For the volumetric estimation of sulphur in special steels, Mr. T. G. ELLIOTT (Sheffield) used the method which was published in the *Journal of the Iron and Steel Institute*, vol. i., 1911. Below is an abbreviated account of his procedure :—

Five grammes of the sample are mixed, as far as practicable, with 0.25 gramme of finely-powdered anhydrous potassium ferro-cyanide, and wrapped in one 11 cm. filter paper if the sample is a graphitic iron, or in two such papers if it is a white iron or a steel, placed in a small porcelain crucible, covered with the lid, and annealed at 750° C. to 850° C. for twenty minutes in a closed muffle. After annealing and subsequent slow cooling outside the muffle, the drillings should still be covered practically completely by the charred filter paper, if the temperature has not been above 850° C., or they have not been in the muffle too long. Low results are obtained if the paper is completely burned away from the top.

After cooling, the contents of the crucible are emptied into a glass mortar, and the slightly caked drillings loosened with a pestle. They are then brushed on to a small piece of stiff paper, which is rolled into a cylindrical shape so that it will fit right into the neck of the evolution flask, and allow of the drillings being transferred to the flask without touching its neck or sides. The evolution flask is connected with a 6" by 1" con-

densing tube containing about 2'' of water, and standing in a conical beaker filled with cold water. A tube from this dips into a flask containing 60 c.c. of a cadmium chloride solution.

This solution is prepared by dissolving 20 grammes of cadmium chloride in water with the aid of a few drops of hydrochloric acid.

Ammonia is added until the precipitate of cadmium hydrate formed completely dissolves. Acetic acid is then added until the solution becomes slightly acid, when a further 20 c.c. are added in excess and the solution made up to 2 litres.

Fifty c.c. of *concentrated* hydrochloric acid are now added, and heat is immediately applied to the flask until the frothing of the contents indicates that solution is well in progress. The flame of the burner used to heat the flask is now lowered. As soon as the speed of the bubbles begins to slacken, the flame of the burner is raised so that the liquid in the flask just boils and the boiling is continued so long as any appreciable amount of gas is given off from the solution. The apparatus is then disconnected, and iodine solution added in excess to the contents of the absorption flask—usually nothing is found in the safety flask—then about 10 c.c. of diluted hydrochloric acid (one part acid to two parts of water) are added, and the liquid shaken to complete the solution of the sulphide. The excess of iodine is then titrated with sodium thiosulphate, starch solution being used as an indicator.

If the filter paper used to wrap the drill or the sulpho-cyanide itself, contain sulphate, the latter are reduced during the annealing and the sulphur given off as sulphuretted hydrogen, so that a blank determination is necessary. This may be conveniently made by treating 5 grammes of "pure" iron in concentrated acid, and another 5 grammes with ferro-cyanide, absorbing the gas from each separately and titrating.

ESTIMATION OF MANGANESE IN STEEL.

ASENITE TITRATION.

Weigh off 0.1 gramme of the sample.

Transfer to a 7" by $\frac{3}{4}$ " test tube.

Weigh off a like quantity of a steel containing a known percentage of manganese.

Transfer to a 7" by $\frac{3}{4}$ " test tube. Treat both of the weighed portions as under:—

Dissolve in 10 c.c. of 1.2 specific gravity hydrochloric acid by heating in a bath of boiling water.

Keep hot till nitrous fumes are driven off and the carbide is dissolved.

Add 5 c.c. of a 0.25 per cent. solution of potassium nitrate and 5 c.c. of a 10 per cent. solution of ammonium persulphate.

Shake well or use a glass plunger to thoroughly mix the solution, and allow to remain for 10 minutes in a bath of water kept at about 70° C.

Transfer the tube and contents to a beaker of cold water.

Titrate with standardised solution of sodium arsenite.

The Sodium Arsenite Solution may be prepared by dissolving about 0.39 gramme of pure arsenious acid and 4 grammes of sodium bicarbonate in water and making up to a litre with water.

The prepared solution may be standardised against a steel containing a known percentage of manganese. If so, it will not be necessary to use standardised steel against each sample or lot of samples.

ESTIMATION OF MANGANESE IN PIG IRON BY THE BISMUTHATE METHOD.

Weigh off 1.1 gramme of the sample.

Transfer to a 500 c.c. beaker.

Weigh off 2 grammes of pig iron containing a known percentage of manganese.

Transfer to a corresponding beaker.

Treat each of the weighed portions as under :—

Add 40 c.c. of 1.2 specific gravity nitric acid, cover the beaker with a clock glass and set on hot plate to dissolve.

Allow to cool.

When cool, add sodium bismuthate until there is a slight excess which settles to the bottom of the beaker. From 0.5 to 1 gramme of bismuthate will be required.

Shake the beaker for a few minutes.

Through a pulp filter or finely-shredded asbestos

filter from graphite and excess bismuthate. The use of a filter pump is advisable.

Collect the filtrate and washings in a conical flask.

Wash well.

From a burette measure the prepared solution required to discharge the colour.

For discharging the colour, sodium arsenite solution (see p. 253) may be used, or the colour may be discharged by measured excess of standardised ferrous-ammonium sulphate and titrated back by standardised permanganate solution. In some works a solution of sodium peroxide in nitric acid is used. This may be prepared by measuring off 160 c.c. of 1.42 specific gravity nitric acid, making up to 1 litre with water and allowing to cool. Into another flask put 5 grammes of sodium peroxide and make up with water to half a litre. Add this solution to the cold nitric acid. Standardise from time to time the resulting solution of hydrogen peroxide against solution of permanganate.

NOTES ON PREPARING AND STORING SOLUTIONS.

The following notes are in addition to those on p. 161 and following pages :—

Arsenious Oxide.—Weigh off 0.66 gramme of pure arsenious oxide (= 0.5 gramme of metallic arsenic) in fine powder, place it in a flask, add 2 grammes of sodium bicarbonate and 100 c.c. of boiling distilled water. Boil the liquid till all the arsenious oxide has dissolved. Allow to cool, add 2 grammes of sodium bicarbonate, and dilute to 1 litre.

Ammonium Thiocyanate (Sulphocyanide) for Copper Estimation.—Dissolve 25 grammes of pure ammonium thiocyanate in water, make up to 250 c.c. with water and mix well. This solution does not keep well.

Bleaching Powder.—Dissolve, as far as practicable, 35 grammes of bleaching powder in 1,000 c.c. of water. Filter into the stock bottle.

Chromic Acid for Carbon Combustions.—Dissolve 50 c.c. of chromic acid crystals in 90 c.c. of water and add 350 c.c. of 1.51 specific gravity sulphuric acid.

Citric Acid—Concentrated Solution.—Dissolve 250 grammes of chemically pure, non-decomposed, crystallised citric acid in water, add 5 grammes of salicylic acid, and make up with more water to $2\frac{1}{2}$ litres.

Citric Acid—Dilute (2 per cent.) Solution.—Dilute 1 part of the above concentrated solution with 4 parts of water.

Copper - potassium Chloride.—See Potassium-cupric Chloride, p. 342.

Dimethylglyoxime for Nickel Estimation.—Pound some crystals of the salt. Weigh off 2.5 grammes and transfer to a 250 c.c. graduated flask. Add about 220 c.c. of 98 per cent. ethyl alcohol, stopper the flask, and shake it till the salt dissolves. If the alcohol has lost strength there will be much difficulty in dissolving.

On long standing, decomposition may take place.

Ether.—This may be purchased as required. It should be kept in a stoppered bottle with a ground cap.

Ferrous Sulphate— $\frac{N}{10}$ Standard Solution for Volumetric Estimation of Vanadium.—Quickly dissolve 1.39 grammes of pure ferrous sulphate in water, to which about 2 per cent. of pure sulphuric acid has been added. Transfer the solution to a

500 c.c. graduated flask, make up to the mark with water, and mix well. Standardise with standard solution of potassium permanganate.

Ferrous Sulphate— $\frac{N}{20}$ Standard Solution for Volumetric Estimation of Vanadium (p. 285).—Carefully dilute a measured quantity of $\frac{N}{10}$ solution, as above, with an equal quantity of water, and mix well.

Iodine Solution for Arsenic Estimation.—Dissolve 2 grammes of potassium iodide in about 200 c.c. of water. In the iodide solution dissolve 1·7 grammes of re-sublimed iodine. Make up with water to 1 litre and mix well. Keep the solution in a dark place for a few days before standardising.

Iodine solution should be kept from light, as far as practicable, and should be re-standardised twice per week, at least, if in regular use; or immediately before using if three days have elapsed since the previous titration.

For details of standardising, see pp. 261 to 263.

Iron Solution for "Correction" in Electrolytic Estimation of Nickel.—Dissolve 0·007 gramme of pure iron wire in hydrochloric acid, and make up with water to 1 litre.

Lead Acetate for Molybdenum Estimation.—Dissolve 10 grammes of pure crystals in about 600 c.c. of water slightly acidulated with acetic acid in a graduated litre flask, make up with water

to the mark, and mix well. 20 c.c. of this solution can precipitate 0.05 gramme of molybdenum as lead molybdate.

Magnesium Citrate.—Place 200 grammes of citric acid, 40 grammes of ammonium chloride, and 200 c.c. of water in a Bohemian flask of 1 litre capacity. Add 500 c.c. of 20 per cent. ammonia liquor. Close the flask with a rubber stopper and allow to remain until the salts have dissolved and the fluid has cooled. Add 55.2 grammes of magnesium chloride, dissolve, and make up with water to 1 litre.

Potassium - cupric Chloride.—Weigh off 90 grammes of pure copper-potassium chloride. Place the weighed portion in a 1,000 c.c. graduated flask along with 50 c.c. of 1.16 specific gravity hydrochloric acid and about 220 c.c. of water. Dissolve the salt, make up to the mark with cold water, and mix well.

Potassium Cyanide- Standard Solution for Nickel Estimation.—This is prepared as directed on pp. 233 to 235.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Combustion.—Dissolve 105 grammes of pure potassium hydroxide in water and make up to 250 c.c. with more water. Keep in a bottle with a tight-fitting cork.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Charging Dufty Tower.—To 200 c.c. of water add 7 sticks (about 80 grammes) of potassium hydroxide. When the solution has cooled transfer it to the Dufty tower.

Potassium Iodide for Nickel Estimation.—Dissolve 20 grammes of pure silver iodide in water, and make up to 1 litre with water.

Potassium Permanganate for Volumetric Estimation of Vanadium.—Dissolve 6.25 grammes of finely-pounded crystals in water in a beaker and stir well with a glass rod without a rubber. Cautiously decant into a 250 c.c. graduated flask. If all the crystals have not dissolved add more water. Decant again. Repeat, if necessary. When all the salt has dissolved, make up with water and mix well.

Potassium Permanganate— $\frac{N}{10}$ Standard Solution for Volumetric Estimation of Vanadium.—Place 3.163 grammes of finely-pounded pure crystals in water in a beaker, and stir well with a glass rod without a rubber. Cautiously decant into a 1,000 c.c. graduated flask. If all the crystals have not dissolved, add more water and decant again. Repeat, if necessary. When all the salt has dissolved, make up with water and mix well.

Silver Nitrate for Nickel Estimation.—Dissolve 0.5 gramme of the pure salt in water, make up to

1 litre with water, and mix well. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate — Standard Solution for Rapid Volumetric Estimation of Nickel.—Dissolve 5.789 grammes of pure silver nitrate in water, make up to 1 litre with water, and mix well. Keep in an amber-coloured bottle or in a dark place.

Sodium Thiosulphate (Sulphocyanide) for Aluminium Estimation.—Dissolve 90 grammes of pure thiosulphate in 50 c.c. of hot water. Filter if necessary. This solution does not keep well.

Starch Solution.—Make 1 gramme of potato starch into a cream with a little cold water.

Boil 500 c.c. of water in an 18 cm. (about 7 inches) diameter porcelain basin. Pour the cream into the boiling water while stirring vigorously. If frothing occurs, blow air over the solution. Boil the solution for two or three minutes, allow it to cool, and add about 6 grammes of zinc chloride in 50 c.c. of cold water, mix well, and, after allowing to settle for a day, decant the clear portion into a stock bottle.

Sulphuric Acid, Dilute No. 1 (sp. gr. 1.51), for the Estimation of Vanadium.—Cautiously pour 500 c.c. of 1.84 specific gravity sulphuric acid into a Bohemian flask containing 500 c.c. of water. Allow to slowly mix and cool. If a precipitate has settled out decant the clear portion of the solution into the stock bottle. Keep in a well-stopped bottle.

Sulphuric Acid, Dilute No. 3, for Use in Rapid Estimation of Lime (p. 353).—Cautiously pour 250 c.c. of 1.84 specific gravity sulphuric acid into 1 litre of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground stopper.

NOTES ON SOME SOLID REAGENTS.

Fusion Mixture.—This is composed of about 6 parts of dry pure potassium carbonate with 5 parts of dry pure sodium carbonate. The mixture may be purchased.

Sodium Peroxide.—This very active reagent, which readily absorbs moisture, is sold in sealed boxes. If transferred to a glass-stoppered bottle the inside of the neck should be carefully wiped with a piece of filter paper before closing with the stopper.

Stead's Tribasic Reagent consists of 20 parts of pure lime or magnesia, 5 parts of potassium carbonate, and 5 parts of sodium carbonate. This is a useful fusion mixture. The two carbonates, soda and potash, when mixed, melt at a lower temperature than when separate, and the magnesia, being infusible, keeps the mass porous and open to oxidation.

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